LATE-GLACIAL TO HOLOCENE CLIMATE VARIABILITY IN WESTERN IRELAND

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In Partial Fulfillment of the Requirements
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Saskatoon

Aaron F. Diefendorf

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Head of the Department of Geological Sciences
University of Saskatchewan
Saskatoon, Saskatchewan S7N 5E2
Canada

UNIVERSITY OF SASKATCHEWAN
College of Graduate Studies and Research

ABSTRACT

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by

Aaron F. Diefendorf

Department of Geological Sciences
University of Saskatchewan
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Examining Committee:

Dr. K. Ansdell	Chair of Graduate Committee
Dr. W. Patterson	Supervisor, Department of Geological Sciences
Dr. C. Holmden	Department of Geological Sciences
Dr. B. Pratt	Department of Geological Sciences
Dr. J. Smol	External Reviewer, Canada Research Chair in Environmental Change, Department of Biology, Queen's University, Kingston, Ontario

Late-Glacial to Holocene Climate Variability in Western Ireland

Increasing concerns over future anthropogenic effects on climate change as a result of increasing greenhouse gases generate concomitant efforts to better characterize recent climate in order to more accurately predict climate in the future. To this end, a multiproxy study of climate variability in western Ireland from lacustrine sediment was undertaken. The interpretation of paleoclimate records derived from lacustrine carbonate minerals is difficult without a good understanding of the mechanisms that generate variation in isotope values of modern surface waters. Variation in surface waters are ultimately incorporated into lacustrine sediment records conflated by temperature. Therefore, a study of the spatial distribution of $\delta^{18}O$ and δD values of lake and river waters from 144 locations in Ireland has been conducted to provide insight into the behavior of lakes and rivers in Ireland, including source, recycling and loss through evapotranspiration. A 7.6 m sediment core was recovered from Lough Inchiquin that provides evidence for rapid and long-term climate change from the Late Glacial to the Holocene. This was determined using carbon and oxygen isotope analyses of lacustrine calcite as well as carbon from bulk organic sediment fractions. Several significant climate perturbations were identified in the $\delta^{18}O_{calcite}$ record such as the Oldest Dryas, Younger Dryas, and the 8.2 ka cold event. A previously undescribed climate anomaly between 7,300 to 6,700 cal. yr B.P. characterized by low $\delta^{18}O_{calcite}$ values with high frequency variability. Variations in carbon isotopes of calcite and bulk organics from the Late Glacial to the Holocene are significant in magnitude (~12‰) and have similar trends that record temporal shifts in the relative contributions of carbon from the weathering of limestone versus the weathering of terrestrial organic matter. $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ suggest a rapid recovery of terrestrial vegetation following the Younger Dryas. Change in $\Delta\delta^{13}C_{calcite - org}$ documents a rapid increase in exogenous fluxes of carbon into the lake at ~9 ka.

Keywords: 8200-yr event, atmospheric circulation, bedrock weathering, charaphytes, County Clare, evapotranspiration, lake sediment, marl, paleoecology, paleolimnology, Polar Front, stable isotopes

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DEDICATION

"We live in a time of renewed perception of climatic and environmental change. For many people this arises from fears about the possibility that man's activities, and their increasing scale and variety, may have side-effects that disturb the climatic regime, just as they are visibly changing other aspects of the environment about us…it is important therefore to seek better knowledge of the pace of climatic change, especially the more rapid and drastic events of climatic history, and to identify the early symptoms which may have signaled the changes. On the other side, study must be given to the flexibility needed in the organization of human society if we are to be able to adjust to such things."

Hubert H. Lamb
Climate History and the Modern World, 1995

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1. INTRODUCTION

1.1 Climate Overview and Motivation

Increasing concerns over anthropogenic influences on climate change as a result of greenhouse gas emissions generate concomitant efforts to better characterize climate of the recent past in order to more accurately predict climate of the future. In addition to defining conditions at a given time in the past, it is important to determine the rate and magnitude of change to best assess the future impacts on human societies and their potential adaptability to abrupt climate change. Global surface temperatures are predicted to warm by as much as 1.4-5.8°C in the next century (IPCC, 2001).

In the last few years, several events in Europe have further increased public awareness of climate change. The 10 warmest years in the instrumental record have occurred since 1990, while the average global temperature of the year 2003 was the second warmest of the last 100 years (NCDC, 2004). During the summer of 2003, Europe experienced some of the highest temperatures recorded since the development of meteorological instruments. France experienced the warmest summer as well, leading to as many as 19,000 heat-related deaths (NCDC, 2004). In addition to increased temperatures, the IPCC (Intergovernmental Panel on Climate Change) has suggested that climate change will likely result in changes in precipitation patterns and increases in the total global precipitation budget. For example, climate models predict that wetter winters will be five times more likely to occur in central and northern Europe (Palmer and Raisanen, 2002). Climate models predict that thermohaline circulation in the Atlantic will decrease in strength and possibly shut down during the next century as a result of anthropogenic forcing, which results from rapid melting of polar ice caps (Broecker, 1997; IPCC, 2001) that could ultimately result in cold atmospheric temperatures.

Global climate models currently predict temperatures that are higher than those observed, suggesting that models may be insufficiently or incorrectly calibrated because appropriate boundary conditions are not available. Comparisons of modeled climate variability with instrumental records demonstrate that climate models underestimate variability (Bell et al., 2000; IPCC, 2001). Furthermore, comparisons of multiple outputs from Coupled Global Climate Models to instrumental records display significant variations that complicate the determination of anthropogenically forced climate variation (Barnett et al., 1996; Barnett, 1999). Higher resolution climate records will establish constraints for models of northern hemisphere climate variability by extending the secular record of comparison for global climate models.

The Holocene has previously been characterized as a period of climatic stability relative to the most recent ice age during which proxy records suggest large amplitude climate variability (Alley et al., 1997). However, other proxy records, such as tree rings (e.g. Epstein and Yapp, 1976; Anderson et al., 1997), lacustrine carbonates (e.g.; Kirby et al., 2001; 2002; Leng and Marshall, 2004), speleothem records (e.g. Baldini et al., 2002), and ice cores (Alley et al., 1993; Dansgaard et al., 1993; NGRIP, 2004) demonstrate significant changes in temperature, precipitation, and atmospheric circulation during the Holocene. Several major excursions occurred during this period, such as the Younger Dryas, 8200-year event, Medieval Warm Period, and the Little Ice Age (Keigwin, 1996; Mann et al., 1999). Several other periods have been identified as well that operate on the multi-centennial time scale that are characterized by major atmospheric circulation changes, polar cooling, tropical aridity, and increased moisture in some regions (Mayewski et al., 2004). Recent research suggests that abrupt large-scale climate change can take place in less than 100 years (Alley et al., 2003). Abrupt climate change in the Northern Hemisphere during the Holocene and Late Glacial has been related to freshwater outbursts associated with deglaciation in North America (Teller et al., 2002; Fisher et al., 2002; Magny and Bégeot, 2004).

Understanding and predicting future climate change requires development of more long-term climate records in order to facilitate construction of a baseline of climate change for climate models to compare with (Barnett et al., 1999). This necessitates a modern spatial reference with which to interface modern analogs with paleoclimate archives (Bowen, 2002) such as speleothems (e.g. McDermott, 2004), ice cores, lacustrine calcite records (Leng and Marshall, 2004), lake sediment cellulose (e.g. Sauer et al., 2001; Wolfe et al., 2001), and trees rings (e.g McCarroll and Loader, 2004).

Climate records that are derived from locations having low continentality are an ideal choice for reconstructing climate records. Continentality can affect climate records because of significant variations in temperature and precipitation associated with seasonal variations in response to differential thermal characteristics of the continent. Therefore, a reconstruction of climate from western Ireland is ideal because it is not affected significantly by continentality (Barry and Chorley, 1987). This allows the development of a climate record that reflects more directly the changes associated with the Atlantic Ocean. Ireland is also an ideal location for lacustrine sediment research because of the distribution of lakes in western Ireland with sediments dominantly composed of calcite (marl).

1.2 Methodology

This body of research will focus on the investigation of climate variability based on a multiproxy record derived from lacustrine sediments from Lough Inchiquin in western Ireland. The thesis is divided into three parts, each a separate article for peer-reviewed publications. Each article is the author's own research including field work, laboratory work, data analysis, and manuscript preparation that incorporates the author's own ideas with guidance from the author's supervisor. Chapter 2 will focus on the distribution of isotopes in surface waters. Surface waters are important as previously outlined to interface modern analogs with paleoclimate archives. This will allow future research to be correlated with the research at Lough Inchiquin. Chapter 3 will focus on the oxygen isotopes derived from lacustrine calcite at Lough Inchiquin and the relation to climate. Chapter 4 will explore carbon isotopes in lacustrine sediment and its relation to vegetational variability and landscape evolution.

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CHAPTER 2. SURVEY OF STABLE ISOTOPE VALUES IN IRISH SURFACE WATERS

2.1 Abstract

We present a study of the spatial distribution of $\delta^{18}O$ and δD values of lake and river waters from 144 locations in Ireland. Before we can gain a better understanding of paleoclimate records derived from lacustrine carbonate minerals we must understand mechanisms that produce variation in isotope values of modern surface waters. The focus of this study is to provide insight into the behavior of lakes and rivers in Ireland, including source, recycling and loss through evapotranspiration. $\delta^{18}O$ values range from –7.4 to –2.4‰ VSMOW, averaging –5.4‰, while δD values range from –53 to –17‰ and average –37‰. The Local Surface Water Line is characterized as $\delta D = 6.24 \bullet \delta^{18}O - 2.93$ ($R^2 = 0.89$). The slope is lower than the Global Meteoric Water Line because these samples are surface waters rather than precipitation samples, thus affected by evaporation that results in values plotting with slopes lower than the GMWL. Samples were also plotted geographically and isotope contour maps were generated of δD, $\delta^{18}O$, and *d-excess* showing several pronounced trends due to water recycling and prevailing wind direction. The effects of evapotranspiration are evaluated to describe the nature of water recycling in Ireland. The short duration of sampling in this project provides a snapshot of modern isotope variability to be applied towards long-term climate change in Ireland and provides a basis of comparison for other proxy records.

2.2 Introduction

Recent studies of Northern Hemisphere Holocene climate reveal that the Holocene is dominated by several climate regimes punctuated by periods of rapid climatic change (e.g., Dansgaard et al. 1993; Alley et al. 1997; Anderson et al. 1997; Fisher et al. 2002). During the summer of 2003, Europe experienced some of the highest temperatures recorded since the development of meteorological instruments. France experienced the warmest summer on record, leading to as many as 14,000 heat-related deaths (NCDC 2004). Furthermore, climate models predict that wetter winters will be five times more likely to occur in central and northern Europe (Palmer and Raisanen 2002) suggesting an increased climate impact on Europeans. Many of these recent increases in northern hemispheric surface temperatures may be partly explained by changes in the North Atlantic Oscillation on decadal time scales that are associated with increasing or decreasing strength of the westerlies (Hurrell 1995; Hurrell et al. 2001). To better understand and help predict future climate change requires development of more long-term paleoclimate records in order to facilitate construction of a baseline of climate change for climate models. This necessitates a modern spatial reference with which to interface modern analogs with paleoclimate archives (Bowen and Wilkinson 2002) such as speleothems, ice cores, lacustrine calcite records, lake sediment cellulose, trees rings, and many other isotope proxies (e.g., Kirby et al. 2001; Sauer 2001; McDermott et al. 2001; Anderson et al. 2002; McFadden et al. 2004; Leng and Marshall 2004).

Lacustrine carbonate records derived from lake sediment cores can provide a diverse suite of information that includes temperature, humidity, precipitation, lake productivity and terrestrial vegetation (e.g., Kirby et al. 2002; McFadden et al. 2004; Leng and Marshall 2004). However, $\delta^{18}O$ records derived from lakes are often dominantly controlled by changes in precipitation that alter $\delta^{18}O$ values of lake water. The influence of changing storm tracks and complicated weather patterns is only beginning to be understood (e.g., Burnett et al. 2004). Continental isotope records frequently display large variation in $\delta^{18}O$ values and are thus likely controlled by changes in the water vapor and temperature of the ocean source area. This large variation may also be caused by changes in temperatures at the precipitation site that may require source area corrections before interpretations are made of isotope proxy records (Grootes 1993). Little research has focused on the distribution of isotopes across a geographic area, but has rather generally focused on climate and $\delta^{18}O$ values of precipitation (Bowen and Wilkinson 2002). $\delta^{18}O$ in precipitation in mid- and high-latitudes correlates well with mean annual surface temperatures (Rozanski et al. 1993). Ultimately, this suggests that changes in climate that alter temperature gradients will alter the resulting isotope value (Fricke 1999). If changes in climate through time alter temperature patterns, then it is not possible to use well-known mean annual temperature models (e.g., Dansgaard 1964) to calculate temperature or $\delta^{18}O$ values in precipitation through the geologic time (Fricke 1999) because these relationships may be incorrect (Bowen and Wilkinson 2002). Detailed analysis of local study areas are needed if the longer geological records are to be realistically interpreted.

Analyses of lacustrine proxy records require detailed local studies of the spatial distribution of isotope values of precipitation and meteoric waters to determine whether lacustrine isotope records are reflective of local or regional climate. Evaluation of modern surface waters is also important in characterizing the degree of isotopic variability across a geographic area. Spatial variations in modern meteoric waters can also be evaluated to determine such climatic parameters as sources of precipitation, transport, recycling of water, and residence times of water bodies. If there are large variations in isotope values across a generally small region, this suggests that climate may be controlled by multiple parameters such as different air masses. Changes in behavior of air masses can play a large role in altering isotope values of precipitation at high latitudes (Fricke 1999). Furthermore, this would suggest that multiple lake cores across this region are required to best characterize regional climate. The record stored in individual lakes will vary depending on differences in depth, area, catchment size, and many other intrinsic and extrinsic factors.

In an ongoing climatological study of Ireland, we relate variation in sediment isotope values to the circumpolar vortex, the Atlantic Ocean, changes in the Gulf Stream and reduced continentality (Chapter 3). A $\delta^{18}O$ calcite record from the late Pleistocene through the Holocene at Lough Inchiquin in western Ireland requires significant variability in $\delta^{18}O$ values of lake water to explain changes in $\delta^{18}O_{calcite}$ values. It is important to determine whether this variability in $\delta^{18}O$ values exists in modern surface waters across the region. If so, this would suggest strong site-specific controls on isotope values of surface waters where low variations in climate exist. With this information in hand, we will have a basis to compare paleolacustrine sediment records and to determine if the lakes of interest are unique or generally representative of regional lakes.

2.3 Study Area

Ireland has a temperate maritime climate where annual changes in temperature are moderated by the proximity of the Atlantic Ocean (Jordan 1997) resulting in low seasonal variation. The influence of the Gulf Stream provides an additional moderating effect on Ireland's climate (Kiely et al. 1998). The mean annual temperature of Ireland is 9.0°C, with average summer maximum temperatures of 19.0°C and average winter minimum temperatures of 2.5°C. Average monthly temperatures at Valentia (Global network for Isotopes in Precipitation), western Ireland vary from 6.9°C in January to 15.1°C in August (IAEA 2001). Average annual rainfall varies from 800 mm to 2800 mm across Ireland with 1mm or more of rain falling 150 days each year, with proportionately more during the summer. The majority of rain is in the southwest, west, and the northwest portions of Ireland (MET 2004) with as much as 1400 to 1600 mm per year (Jordan 1997). The probability of days with rain in western Ireland during summer months can be up to 50% and during winter months as high as 80% (Kiely 1998). Relative humidity in Ireland is generally high, averaging between 70% and 90% (MET 2004). In the more central western part of Ireland, climate is very similar to the Valentia IAEA site with higher annual rainfall than the rest of Ireland.

Rainfall data has been tracked at Valentia since 1957 as part of the IAEA project on collecting isotopes in precipitation. Meteorological data were grouped monthly with arithmetic mean, minima, and maxima calculated each month (Fig. 2.1). Mean monthly precipitation at this site varies from 166 mm in January to 81 mm in June. Winter months contribute a major component of total annual precipitation, occasionally twice that of summer. Temperature is highest in July and August averaging 15.0°C. A gradual decrease occurs to the coolest temperatures in January of ~7.0°C. This rather small variability in temperatures for such high latitudes is due to proximity of the Atlantic Ocean, which moderates Ireland's climate.

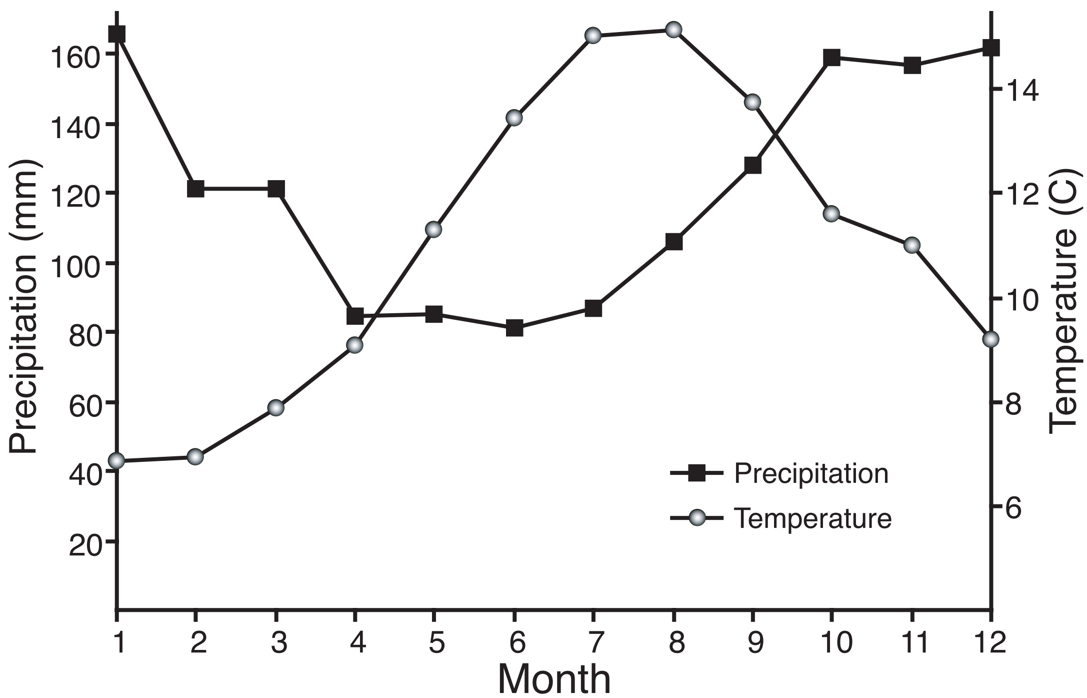

Figure 2.1. Valentia, Ireland GNIP monthly averaged precipitation and temperature data from the years 1957 to 2001. The summer is characterized by highest temperatures and lowest rainfall.

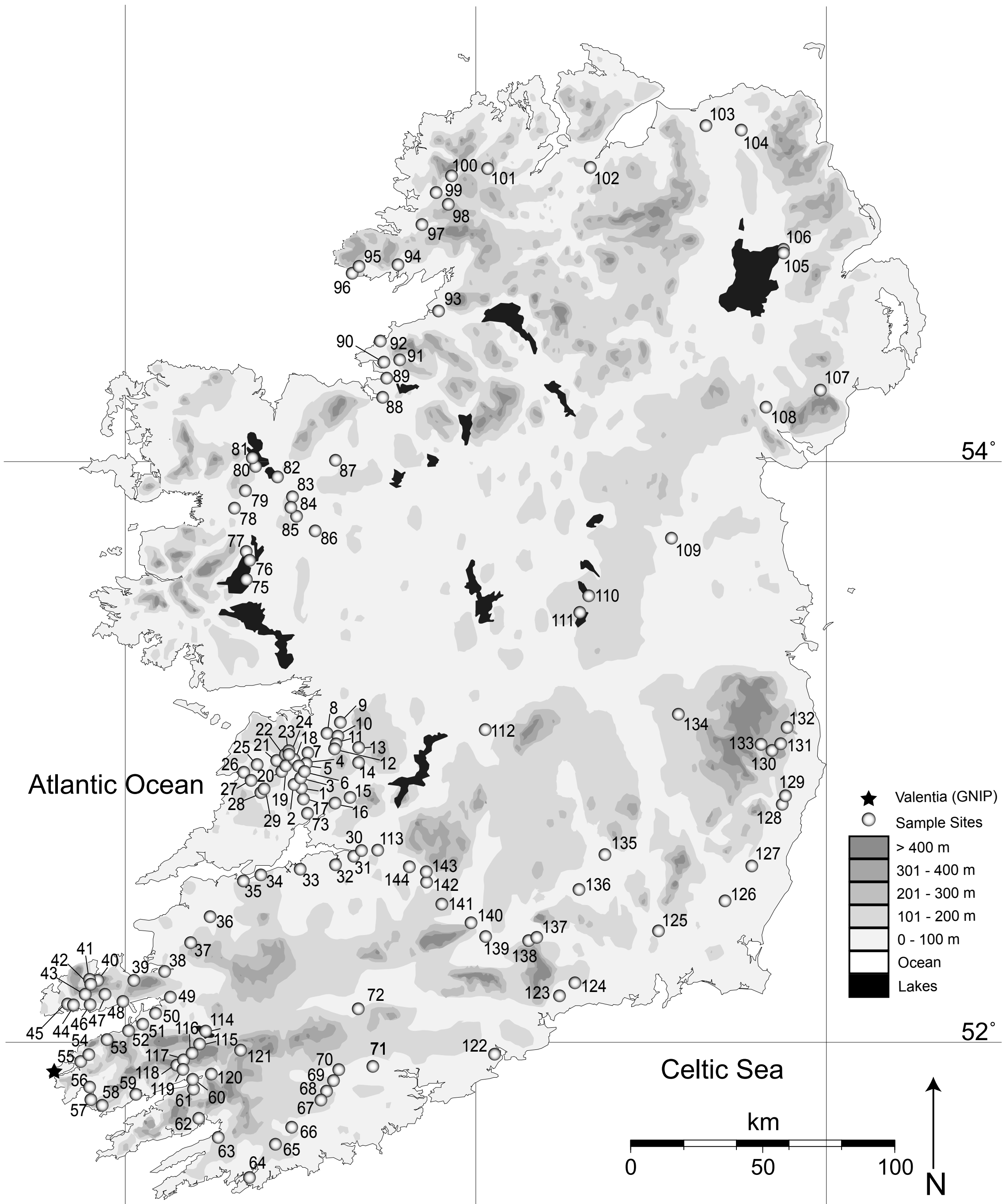

Figure 2.2. Locations and respective numbers of surface water sample sites in Ireland. The Ireland GNIP collection site at Valentia is marked with a star. Elevation contours are shown as well for comparison.

2.4 Methods

Samples were collected in Ireland during June and July of 2003 (Fig. 2.2, see Appendix A). Water was collected using 30 or 60 ml Nalgene® bottles. Sample locations were established using a Magellan® GPS and Ireland Ordnance Survey topographic maps at a scale of 1:50,000. Sample names were recorded using the original Gaeilge (Irish Gaelic).

δD and $\delta^{18}O$ values were determined using a continuous flow pyrolysis technique. Aliquots of 1 μL of water are injected via a septa into a Finnigan MAT TC/EA via a GC PAL® auto-sampler using a 10 μL syringe. Water is vaporized in a ceramic column lined with glassy carbon and packed with glassy carbon fragments at 1450°C and reduced to CO and H_2 gases. These gases are passed through the system using ultra-high purity helium as the carrier gas. Gases exiting the column are separated in a 5Å molecular sieve gas chromatograph at 90°C followed by a Conflo III interface/ open split for helium dilution. CO and H_2 gases are measured on a Finnigan MAT Delta Plus XL mass spectrometer relative to reference gases from the dual inlet port. Samples are analyzed using four internal standards (characterized by VSMOW, VSLAP, and GISP). Multiple injections are employed to minimize any memory effect associated with needle contamination or with the glassy carbon reactor. Data reduction is conducted using a two-point calibration with two of the internal standards, corrected for drift using a third internal standard (normally less than 1‰ on $\delta^{18}O$ and 2‰ on δD throughout a run), and the fourth internal standard is used as a check to determine run reproducibility. Sample precision is determined to be ±0.3‰ for $\delta^{18}O$ and ±3.0‰ for δD (1σ, n=45) using an internal standard and all values are reported relative to VSMOW.

2.5 Results and Discussion

2.5.1 IAEA/GNIP Precipitation at Valentia

Data were obtained from the IAEA station in Valentia to determine long-term changes in precipitation in Ireland and as a general comparison to regional water sampling at lower temporal resolutions (IAEA 2001). The IAEA site measured temperature, precipitation, tritium, δD, and $\delta^{18}O$ values from most months encompassing the years between 1957 and 2002. Although these data are only available for the Valentia station in the southwestern part of Ireland, they provide a framework for initial investigations into precipitation isotope data and ultimately surface water in Ireland.

A total of 339 monthly averaged samples for both δD and $\delta^{18}O$ were taken during this period by the IAEA and a local meteoric water line (LMWL) was calculated from the δD and $\delta^{18}O$ values (Craig 1961; Dansgaard 1964) and is reported in Figure 2.3. The best-fit regression line (least squares assuming low standard error) for the data is described by an equation for the LMWL of $\delta D = 6.86\ (\pm 0.13) \bullet \delta^{18}O + 1.97\ (\pm 0.71)$ (r=0.94, n=339). Long-term monthly averages were also calculated, as well as the minimum and maximum value for each month (Fig 2.4), with

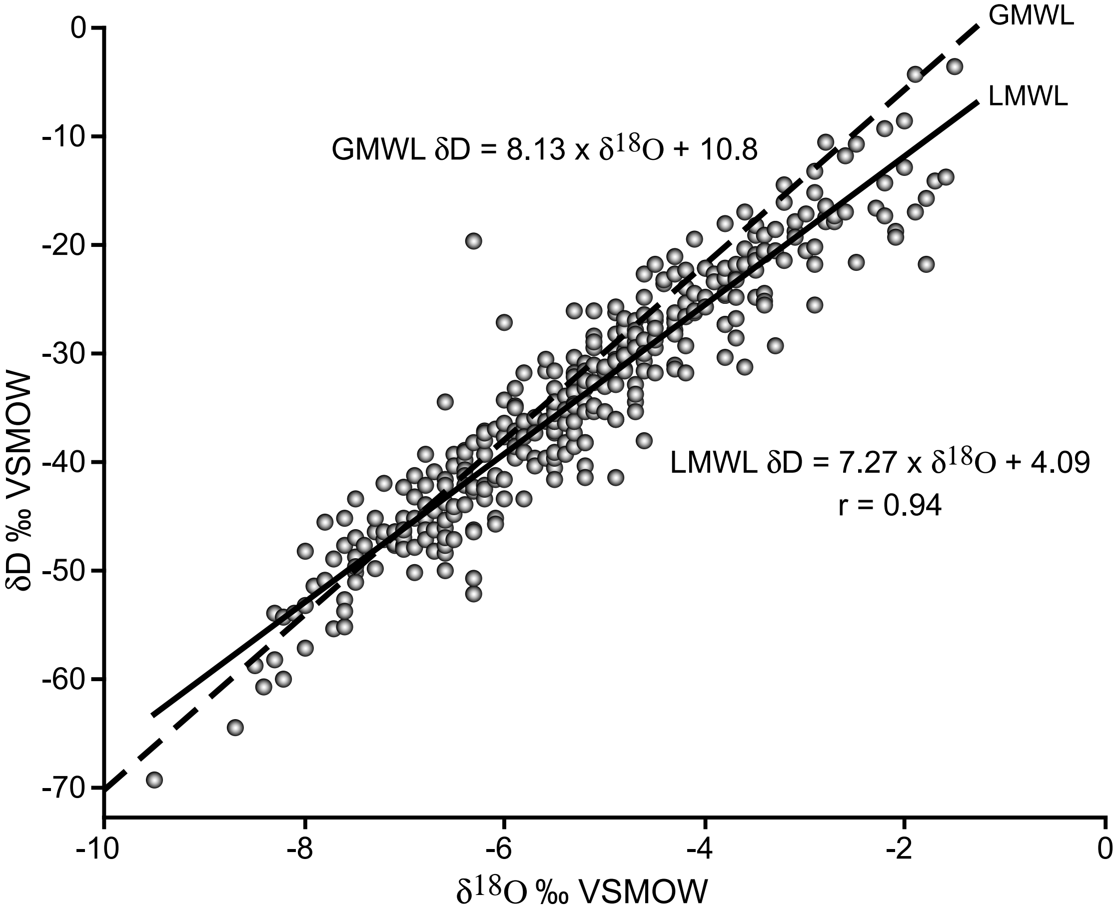

Figure 2.3. Isotopes in precipitation at the GNIP site in Valentia. Samples are averaged monthly. A LMWL (solid line) and a GMWL (dashed line) are for comparison.

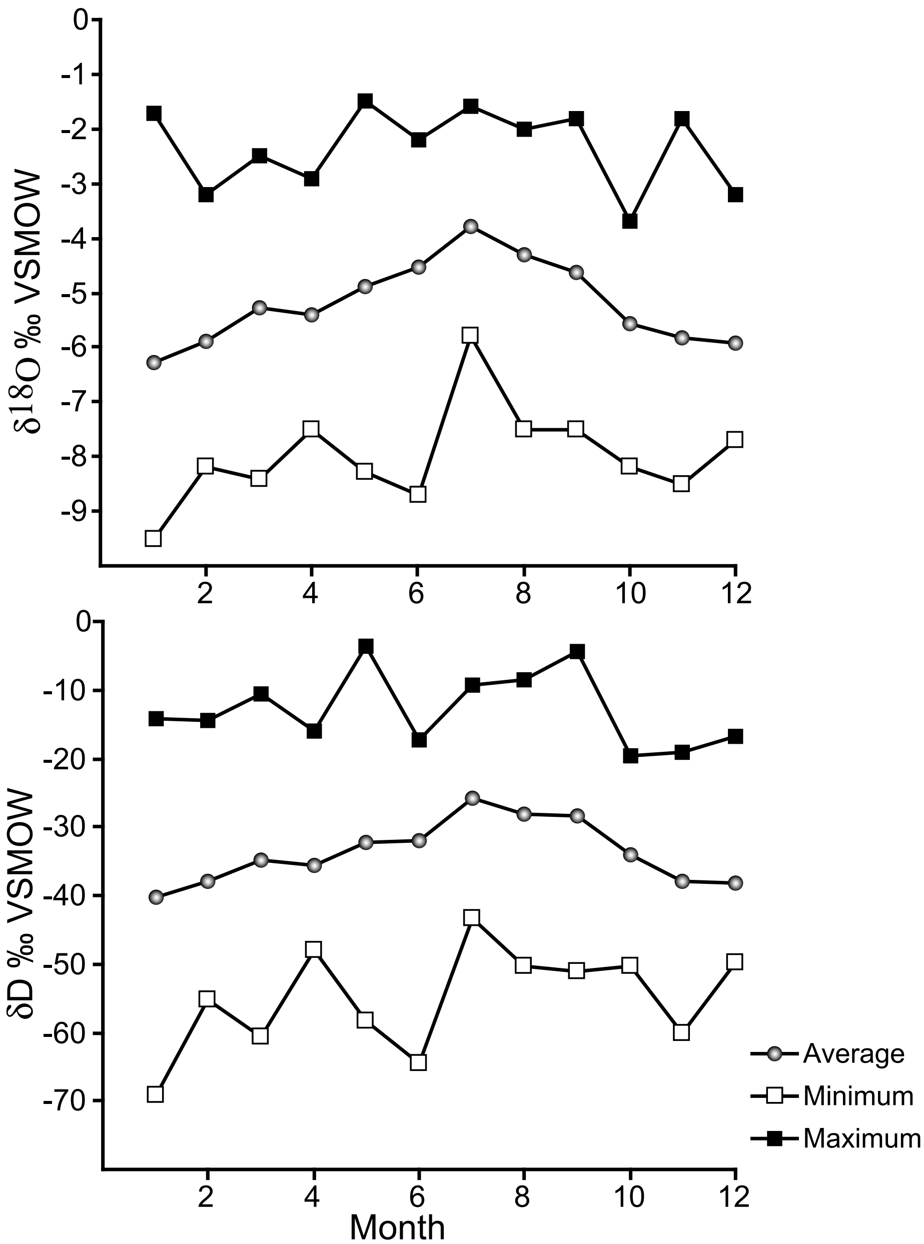

Figure 2.4. Monthly averaged isotopes in precipitation at the GNIP site in Valentia for $\delta^{18}O$ and δD.

precipitation varying by 3.6‰ to 15.5‰ in $\delta^{18}O$ and δD respectively. However, variations between minimum and maximum values for each month can be significant. This range in values is most extreme in January with a difference of –7.8‰ in $\delta^{18}O$ and –55‰ in δD. This can be attributed to an increased frequency of storms, decreased temperatures, and increased snow during winter months. Winter values are lower than summer values due to lower condensation temperatures. As a result, greater fractionation of isotopes occurs as proposed by Dansgaard (1964) and Rozanski et al. (1993).

The deuterium excess ($d = \delta D - 8 \bullet \delta^{18}O$; Dansgaard 1964) has been previously studied by Rozanski et al. (1993) for Valentia. Monthly d-excess values have been calculated from the IAEA data set at Valentia (Figure 2.5): mean values range from 4.5 to 10.5‰ with the highest values occurring in the winter and the lowest values occurring in the summer. The largest variability in monthly d-excess values occurs during the winter months. Differences in d-excess values between summer and winter months are caused by two main factors: lower relative humidity in the source region (Atlantic Ocean) during evaporation of the source waters imparting a kinetic fractionation of the vapor during the winter months and lower relative humidity in summer months causing partial evaporation of raindrops during precipitation events (Rozanski et al. 1993). This causes the LMWL to have a slope less than 8 due to this bimodal distribution of isotope values (Rozanski et al. 1993).

2.5.2 Surface Water Data Results and Discussion

Samples were collected during a three-week period in June and July, thus reflecting low temporal resolution, but may be considered as a snapshot of stable isotope values of surface waters for one season. A few samples were taken at sites that appeared in the field to have a tidal influence and therefore may have an isotopic signal influenced by seawater (samples 38, 102, and 122 not used in data analysis).

Surface water $\delta^{18}O$ values range from –7.4 to –2.4‰, averaging –5.4‰, and δD values ranging from –53 to –17‰, averaging –37‰. Sample values were separated into lakes, rivers unrelated to lakes (not downstream), rivers downstream of lakes, and reservoirs. Linear regressions (least squares assuming low standard error) were calculated for each group of data (except reservoirs) and equations are shown on Figure 2.6. The slopes all have equations that are lower than the GMWL and a majority of the data plot below the GMWL. A study of fresh waters in the British Isles also records similar results, although the number of surface waters is low (Darling et al. 2003). The slopes are all lower than the GMWL because surface waters are affected by evaporation that results in values plotting with lower slopes than the GMWL. As expected, lakes have the lowest slope of all the surface waters. Lakes have lower slopes than rivers in part due to increased residence time (Gibson et al. 2002) resulting in greater evaporation, thus causing values to be

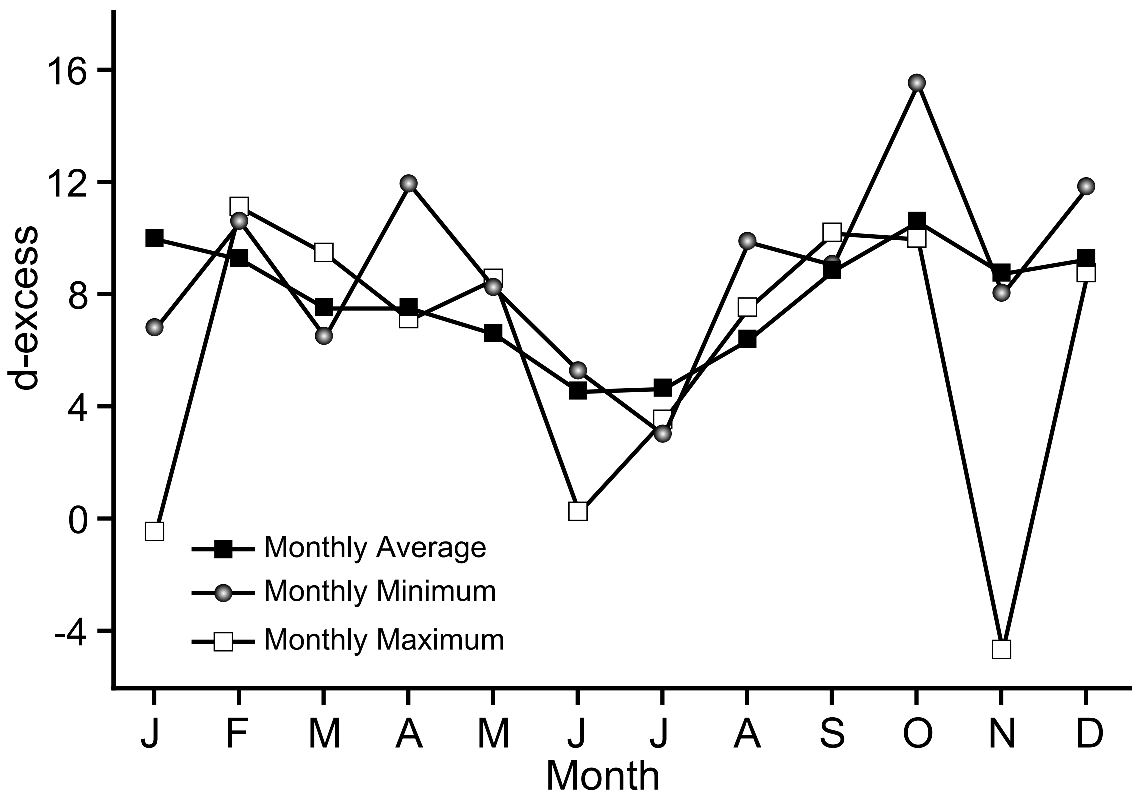

Figure 2.5. Monthly averaged d-excess values from in precipitation at the GNIP Valentia.

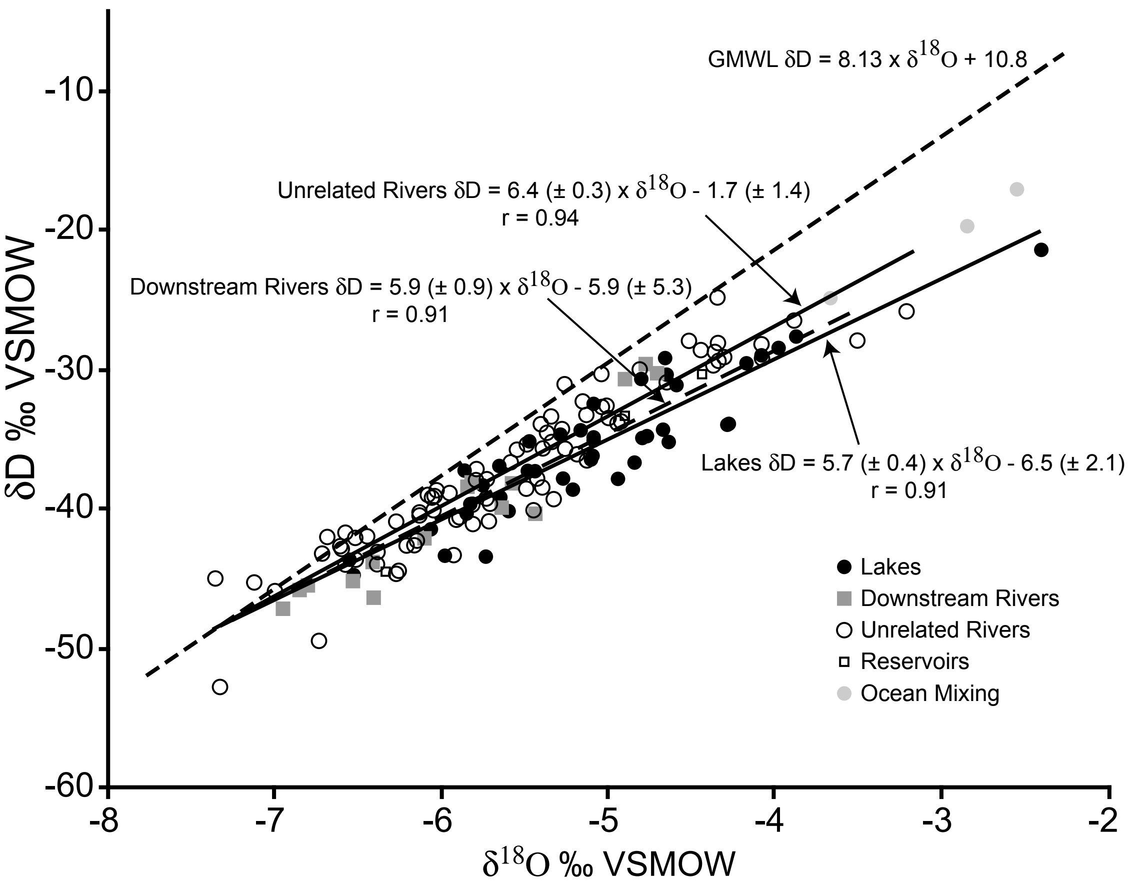

Figure 2.6. $\delta^{18}O$ and δD values of types of surface waters in Ireland and their respective best fit equations and are compared to the GMWL.

higher due to preferential evaporation of $H_2{}^{16}O$. Initially, we were surprised that downstream rivers had a slope higher than lakes (7.6±0.6) because downstream rivers should have characteristics more in common with lakes. However, after closer examination of the data, these differences are caused by the 3 highest samples (41, 42, and 52), which are the only downstream rivers located in the southwest of Ireland (Kerry Peninsula). These three sites affect the slope because of the higher humidity and higher rainfall due to the proximity of the Atlantic Ocean. After removing these three values, the downstream rivers have an equation that is the same as the lakes (within tolerances) and is shown on Figure 2.6.

Samples were also plotted geographically with ranges outlined for $\delta^{18}O$, δD, and d-excess values (Fig. 2.7, 2.8, 2.9). δD and $\delta^{18}O$ have similar contours as expected due to the same processes controlling both isotopes. However, there is a larger effect on δD values due to increased kinetic fractionation. Contour lines are closest along the west coast and become further apart inland. Surface water values across Ireland exhibit several general trends. δD and $\delta^{18}O$ values are significantly higher in western Ireland decreasing to the east. This correlates to general precipitation trends with prevailing winds coming from the southwest (Kiely et al. 1998). Isotope values decrease to the east due to progressive distillation of air masses as rain tracks west to east.

There does appear to be a correlation between altitude and isotope values of surface waters. However, integral stream head altitude was not factored into this study and therefore a more rigorous comparison was not attempted at this time. Altitude isotope effects are generated by adiabatic cooling and resultant isotopic fractionation during rainout of precipitation. Thus, higher altitude regions of Ireland generally correlate with lower isotope values. Some general altitude effects may be seen in the Kerry Peninsula where $\delta^{18}O$ values range from –3.9 along the coast to –5.5‰ further inland on the peninsula. This corresponds to a change in altitude of about 600m or 0.27‰ per meter, within the general altitude effect of –0.15 to –0.5‰ per meter (Clark and Fritz 1997). Because few mountains in Ireland are higher than 1000m, altitude effects are mostly localized.

2.5.3 The Burren Watershed

The Burren region of County Clare in western Ireland is of considerable interest due to its unique ecological, archaeological, and climatological setting (Drew and Magee 1994). Although the region covers less than one percent of the land surface of Ireland, more than half of the country's native species of flora are found there (Drew 1994). Geology is dominated by Lower Carboniferous limestone deposited in shallow equatorial seas (Moles and Moles 2002). Since the last glacial maximum, ~17,400 cal. yr B.P. in Ireland (Bowen et al. 2002), many areas of this region have remained non-vegetated due to the lack of soil formation in the higher areas and only moderate soil formation in the valleys. Moles and Moles (2002) have undertaken detailed studies of the Burren's soils to determine soil processes, accounting for the loss of the region's soils and to

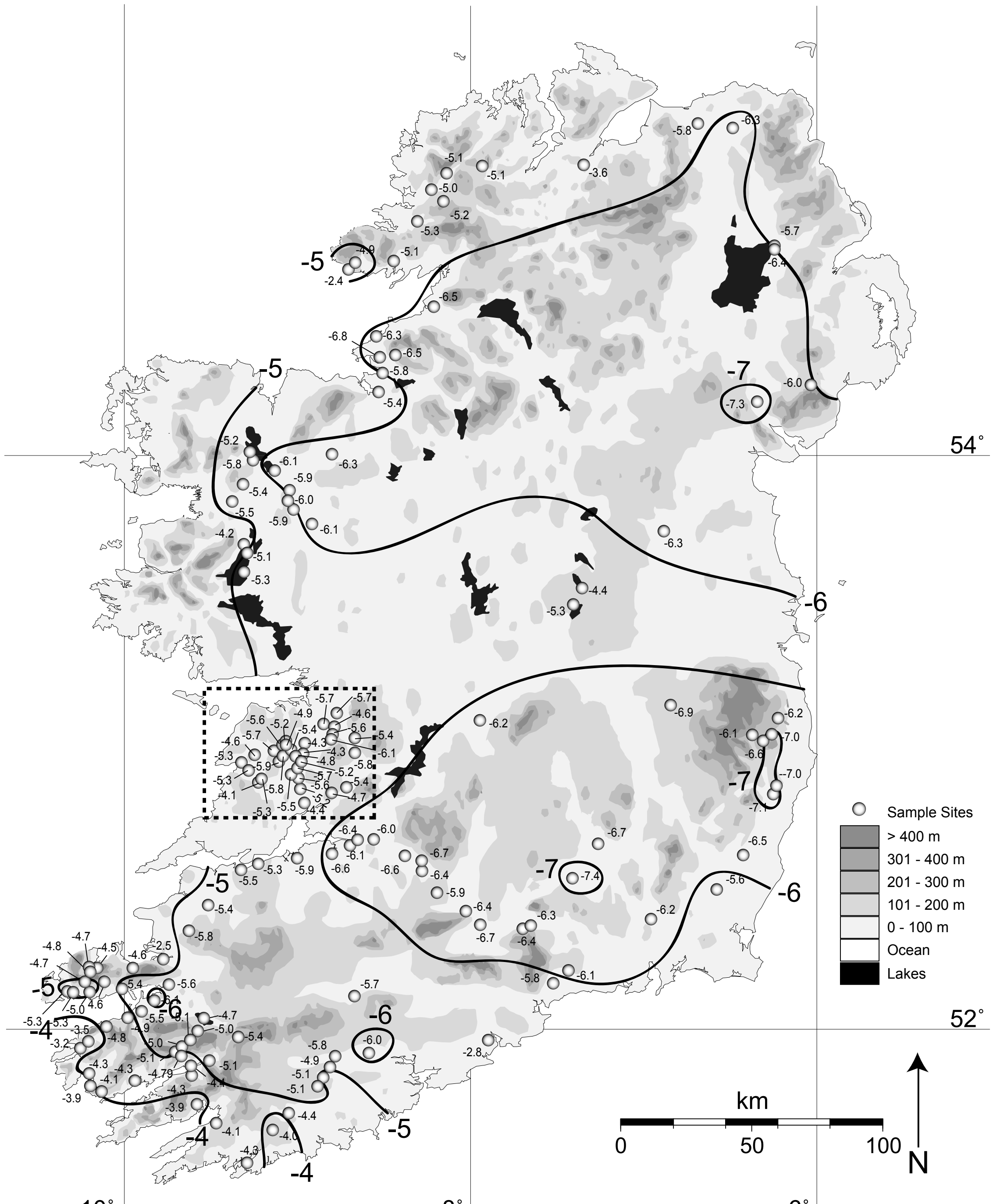

Figure 2.7. Contour line of δ^{18}O in Irish surface waters with sample values next to positions. All values are in ‰ VSMOW. Detailed map of surface waters of The Burren, dashed box, are shown in Figure 2.9.

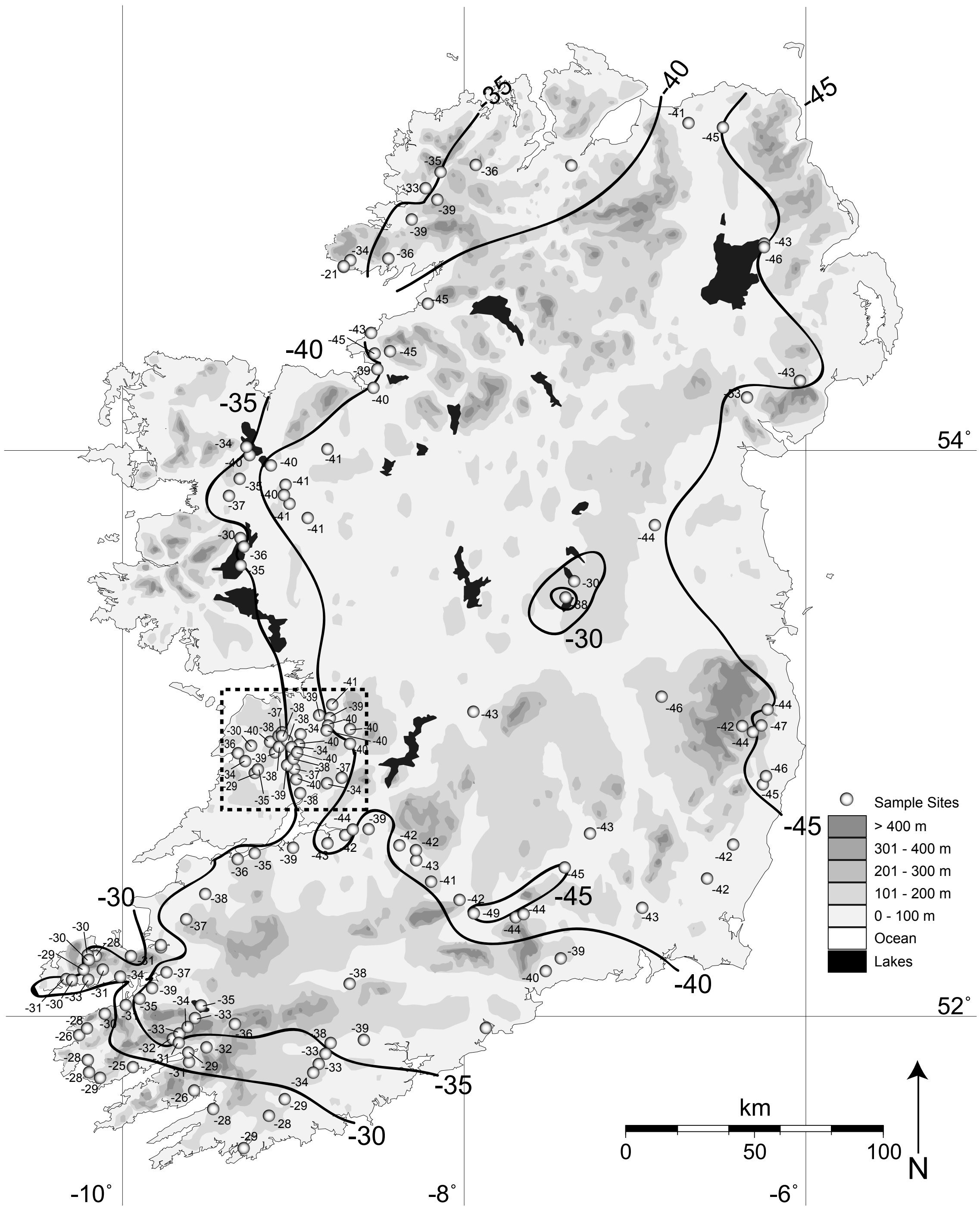

Figure 2.8. Contour line of δD in Irish surface waters with sample values next to positions. All values are in ‰ VSMOW. Detailed map of surface waters of The Burren, dashed box, are shown in Figure 2.9.

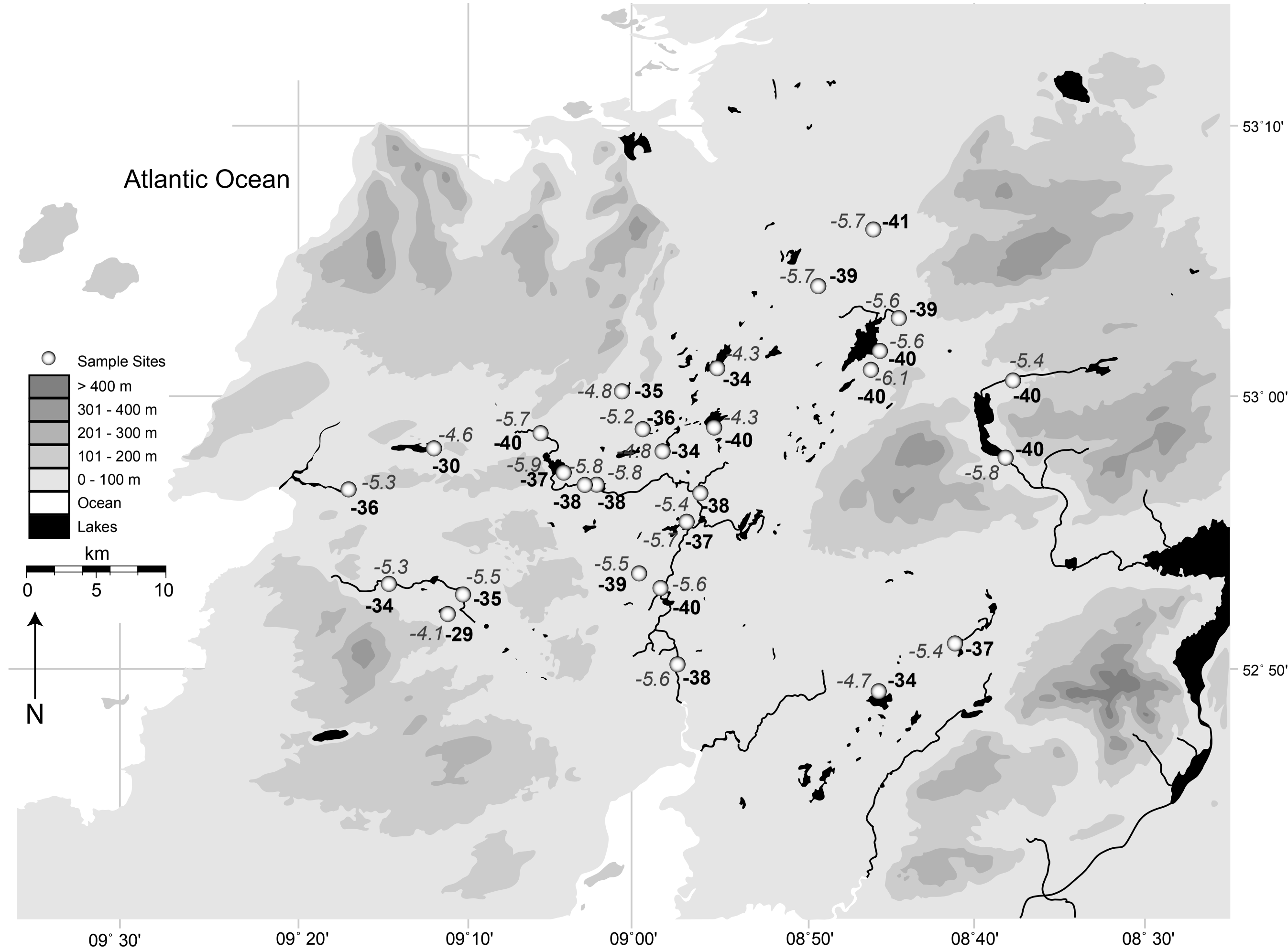

Figure 2.9. Map of $\delta^{18}O$ and δD values of The Burren region in ‰ VSMOW. $\delta^{18}O$ values are in italics and δD values in bold.

develop future management practices for The Burren National Park. Burren hydrology is not well understood due to the complicated karstic nature of the region (Drew 1990) Furthermore, few studies have examined the numerous lakes in a regional context. To date, studies have been confined to temperature, dissolved oxygen, and heat budgets of only a few of the numerous lakes (Allott 1986). Additionally, this region has numerous seasonal lakes called turloughs that are found in regions underlain by limestone that generally flood in the autumn and drain through swallow holes by spring (Coxon 1987). Lakes of the Burren contain superb high-resolution records of climate change. However, to better understand the meaning of carbonate sediment isotope values requires a better understanding of regional hydrology and the intricacies displayed by individual lakes. To our knowledge, stable isotope values of surface waters in this region have not been previously determined.

We sampled 31 lakes and rivers within this region (Fig. 2.9) to determine a general distribution and variation of isotope values. Turloughs were not sampled because they are generally dry during the summer. Of the 31 lakes and rivers sampled, the overall variation was between 1.8‰ in $\delta^{18}O$ and 7‰ in δD. These variations do not seem to follow a general pattern or trend. This may be in part due to variations in the residence time of these lakes and the extent/orientation of the catchment regions. Altitude variation in this region is limited to ~300m therefore contributing very little to isotope variability. Along the largest and longest rivers in this region, the Fergus, isotope values are essentially invariant. The upstream value to the north has an initial $\delta^{18}O$ value of –5.7‰ with only a slight increase to –5.4‰ along the flowpath, corresponding to input from a tributary with higher values. This tributary derives its source water from a different area that we interpret to have increased evaporation effects and/or longer residence time. This is the most reasonable scenario because some of the highest values in this region are just north of this tributary. Values decrease slightly towards the south end of the Fergus River before draining into the Shannon River.

2.5.4 Evapotranspiration

To best understand the regional distribution of isotopes in surface waters, it is important to be aware of the origin of the source water. The two main sources of water for precipitation, other than oceans, are continental sources in the form of transpiration from plants and evaporation from large lakes (Ziegler 1989). Surface waters dominantly come from precipitation and a significant percentage of this may come from evapotranspiration. Evapotranspiration has been demonstrated in other parts of the world that such processes are significant and sources sometimes include lake effect snow (Burnett et al. 2003). One method to quantify the amount of evapotranspiration is to use the d-excess (Dansgaard 1964). The d-excess is defined by the amount of “extra” deuterium from relating the $\delta^{18}O$ and δD. It is controlled by kinetic fractionation during evaporation of surface waters because average humidity is always lower than 100%. As humidity decreases, kinetic fractionation increases. As surface water evaporates, an increase in δD and $\delta^{18}O$ values results. However, this occurs to a greater degree for deuterium because of the greater mass difference between H and D compared to ^{16}O and ^{18}O (Clark and Fritz 1997). As vapor is recycled, the d-excess increases in response to greater proportions of evaporate content (Fröhlich et al. 2002). When water is lost by evaporation, the d-excess will decrease. Other factors that may contribute to differences in d-excess include changes in physical conditions such as humidity, air temperature, and sea surface temperature of the source area (Fröhlich et al. 2002).

Surface water d-excess values for Ireland were determined from the data. The average d-excess value for Ireland is 6.6‰, below the world average of 10‰. However, the LMWL for Ireland falls below a slope of 8 suggesting that d-excess should be slightly lower. A contour map of d-excess values was generated for Ireland that shows highest values in the southwestern portion of Ireland, including the Wicklow Mountains and in southeastern Ireland with values around 10‰ (Fig. 2.10). Values in the north are somewhat lower than in the south. It is also important to keep in mind the standard deviation imparted by this sampling method results in d-excess values having a standard deviation of ±3.1‰.

Evapotranspiration has previously been modeled in Ireland by Mills (2000) using meteorological variables that include precipitation, temperature and sunshine hours employing a dataset from 1961 to 1990. From six sites in Ireland where potential evapotranspiration was actually measured, it appears that it is the highest in the summer months ranging from approximately 60 to 95 mm. Values in the winter were significantly lower with quantities around 5 to 15mm. Mills' model estimated actual evapotranspiration as a percentage of the annual precipitation across Ireland using a 5 X 5 km grid and then generated a contour map. The contour lines show that the entire west coast of Ireland has nearly half the evapotranspiration of eastern Ireland. Our d-excess contour lines compare favorably to those of Mills, except in the southwest. More interestingly, our data demonstrate that much of the southwest and southeast regions have similar d-excess values. This is surprising because we expected that the southeastern portion of Ireland to have lower d-excess values due to the increase in evapotranspiration (assuming a significant portion of this is evaporation). This could be explained by a larger proportion of the evapotranspiration in southeast Ireland being derived from transpiration, resulting in d-excess values that are not much different than the southwest (transpiration does not result in a significant fractionation of water isotopes). However, a more likely scenario for the lack of variation in the south of Ireland may be due to significant input from cyclones that form over the Atlantic Ocean and then travel across Ireland. If recycling of waters occurs, it is likely mixing with these large cyclonic systems during advection. This could moderate or overwhelm isotope recycling signatures. Furthermore, if evaporation has any effect on d-excess values, it is likely small due to the high humidity year round (usually greater than 85%) causing a small amount of kinetic fractionation.

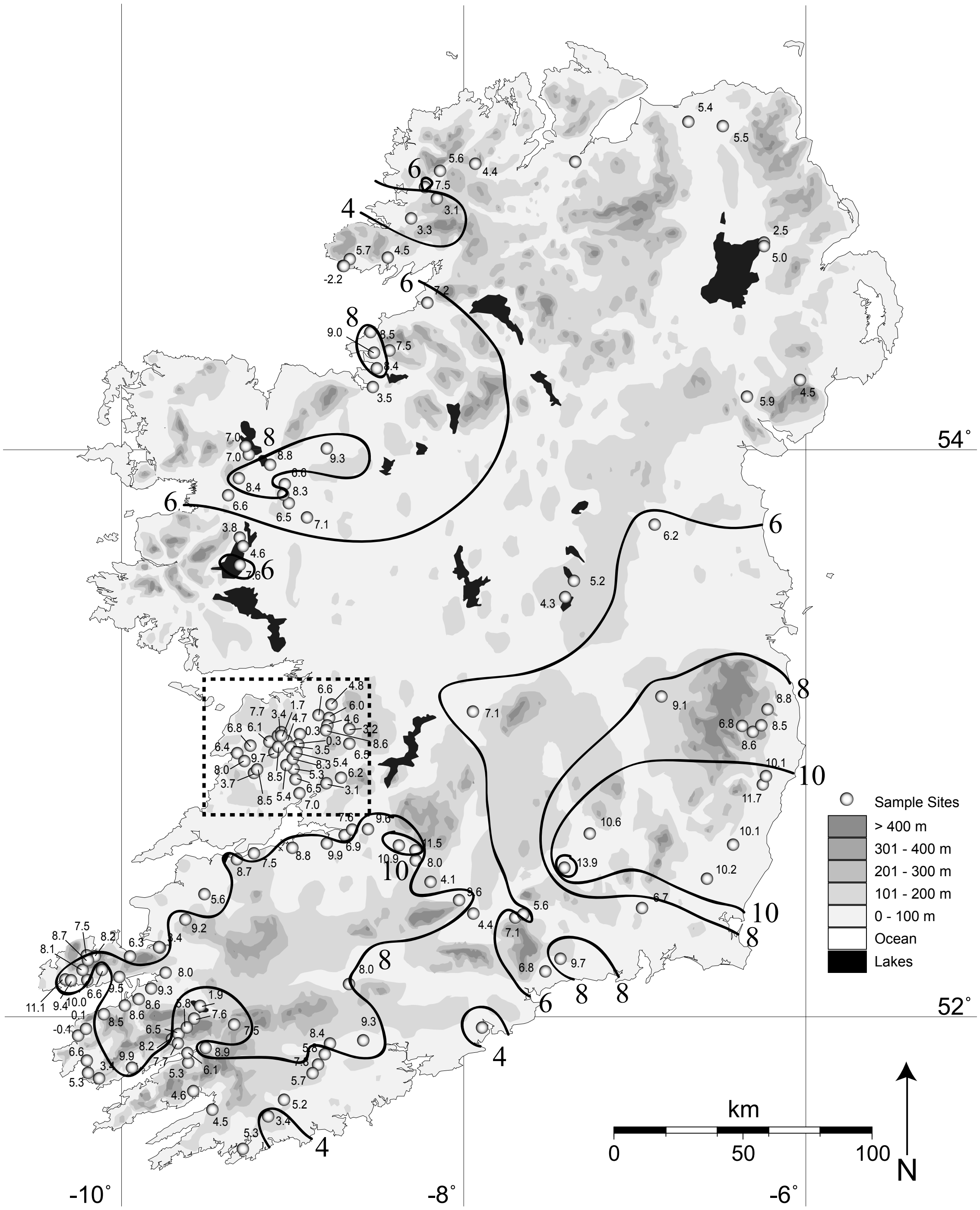

Figure 2.10. Contour line of d-excess in Irish surface waters with sample values next to positions. Burren region (denoted in dashed box) was not included in determination of positions of contour lines due to the complexity of the region.

2.5.5 Implications for Sediment Based Research

The spatial variation of surface waters in the modern is defined by atmospheric circulation, which controls the atmospheric temperature, source of moisture, humidity, and moisture trajectory. Moisture trajectory of air masses is important in regions where orographic effects, moisture recycling, and additional sources of moisture modify isotope values. Changes in atmospheric circulation through time will alter the spatial variation of surface waters. This is significant when studying the long-term variation in isotope values of lacustrine sediment records. For example, variations in isotope values of surface waters in Ireland are more frequent in the southwest where isotope contour lines are closer together indicating a higher isotope gradient (e.g., Fig. 2.7). If atmospheric circulation was shifted so that air masses are predominantly derived from the southeast, then the isotope gradient would be greater in the southeast than the southwest. This would result in higher isotope values in the southeast reflecting closer proximity to the source of moisture. This is significant over the Holocene where atmospheric circulation has deviated from the present such as during the 8.2 ka event where the jet stream was shifted south resulting in less precipitation in Ireland (Magny and Bégeot 2004).

Spatial variations of isotopes are important in interpreting lake sediments at Lough Inchiquin (sample location 20, Fig. 2.2) in western Ireland. The distribution of surface waters (Fig. 2.7) suggests that $\delta^{18}O$ values in this region are similar with values averaging 5‰ with prevailing storm tracks from the southwest. If atmospheric circulation changes such that the prevailing storm tracks are from the west, $\delta^{18}O$ values would be more similar to coastal values such as modern values are in the southwest. The extreme case would be if storm tracks alter to come from the east which would significantly modified $\delta^{18}O$ values such that values in western Ireland would be more similar to modern values in the east of ~6‰. This spatial variation urges caution in using simplified models for the interpretation of lake marl isotope data.

For example, comparison of sediment isotope records between east and west would suggest that temperatures in the east would be 4.2°C warmer than in the west because the water values are 1‰ lower in the east. This study encourages generation of surface water data sets for use in the interpretation of lake sediment data in all areas. Differences in contemporaneously precipitated carbonate in geographically spaced locations can generate records of changes in spatial variations through time, which can be used to produce paleo-circulation maps through the Holocene.

2.6 Conclusion

This study provides a first regional survey of surface water isotope values for Ireland that are useful for characterizing modern meteorological behavior and providing a template for comparison with lake sediment-based paleoclimate records. Significant variation in isotope values suggest that climate records derived from sediment isotope values need to be evaluated in a regional context if applications to global models are to be realistic. In the Burren region of county Clare, variation in lake values suggest that factors in addition to precipitation are significant in determining the values of individual lakes. These factors likely include differences in residence times, catchment size, evaporation, and many other factors. Therefore, future studies of climate change would provide the most comprehensive record by using several different types of lakes, each of which shows differential sensitivity to different meteorological parameters.

2.7 Acknowledgements

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2.9 Manuscript's Relationship to the Thesis

Chapter 2 presents a record of the spatial variation of stable isotope values of surface waters across Ireland. This is related to the thesis by establishing a framework for comparison to spatial

CHAPTER 3. EVIDENCE FOR HIGH FREQUENCY LATE GLACIAL TO MID-HOLOCENE (16,800 TO 5,500 CALENDAR YEARS BP) CLIMATE VARIABILITY FROM OXYGEN ISOTOPE VALUES OF LOUGH INCHIQUIN, IRELAND

3.1 Abstract

A 7.6 m core recovered from Lough Inchiquin, western Ireland provides evidence for rapid and long term climate change from the Late Glacial to the Mid-Holocene. We determined percentage of carbonate, total organic matter, mineralogy, and $\delta^{18}O_{calcite}$ values to provide the first high-resolution record of climate variability for this period in Ireland. Following deglaciation, rapid climate amelioration precedes large increases in GISP2 $\delta^{18}O_{ice}$ values by ~2,300 years. A brief cold period (previously unidentified in Ireland) punctuates the warming period at ~16,000 cal yr B.P. The Oldest Dryas (15,100 to 14,500 cal yr B.P.) is the most significant Late Glacial event in our record. Brief warming at ~12,700 cal yr B.P. is followed by characteristic Younger Dryas climate conditions. A rapid increase at ~10,500 cal yr B.P. marks onset of the Boreal warming in western Ireland. The 8,200 cal yr B.P. event is represented by a brief cooling in our record. Prior to general warming, a larger and previously undescribed climate anomaly between 7,300 to 6,700 cal yr B.P. is characterized by low $\delta^{18}O_{calcite}$ values with high frequency variability.

3.2 Introduction

Concern over anthropogenic forcing of climate related to increasing greenhouse gases has generated significant international efforts to better understand the rate, timing, and magnitude of climate change. Recent research suggests that abrupt large-scale climate change can take place in less than 100 years (Alley et al., 2003). In the last few years, several events in Europe have further increased public awareness of climate change. The 10 warmest years in the instrumental record have occurred since 1990, while the average global temperature of the year 2003 was the second warmest of the last 100 years (NCDC, 2004). In addition to increased temperatures, the IPCC (Intergovernmental Panel on Climate Change) has suggested that climate change will likely result in changes in precipitation patterns and increases in the total global precipitation budget. Furthermore, climate models predict that thermohaline circulation in the Atlantic will decrease in strength and possibly shut down during the next century as a result of anthropogenic forcing that results in rapid melting of polar ice caps (Broecker, 1997; IPCC, 2001).

Global surface temperatures are predicted to warm by as much as 1.4-5.8°C in the next century (IPCC, 2001). However, global climate models currently predict temperatures that are higher than those observed, suggesting that models may be insufficiently or incorrectly calibrated because appropriate boundary conditions are not available. Higher resolution climate records will better constrain models of northern hemisphere climate variability. The Holocene has previously been characterized as a period of climatic stability relative to the most recent ice age during which proxy records suggest large amplitude climate variability (Alley et al., 1997). However, further analysis of multiple proxy records, such as tree rings (e.g. Epstein and Yapp, 1976), lacustrine carbonates (e.g. Leng and Marshall, 2004), speleothem records (e.g. Baldini et al., 2002), and ice cores demonstrate significant changes in temperature and precipitation during the Holocene (Alley et al., 1993; Dansgaard et al., 1993). Several major excursions occurred over this period such as the Younger Dryas, 8200-year event, Medieval Warm Period and the Little Ice Age (Keigwin, 1996; Mann et al., 1999).

Lacustrine calcite (marl) has long been established as a reliable climate proxy (e.g. Leng and Marshall, 2004). Paleoclimate reconstructions from lake cores in the northeastern United States have demonstrated that oxygen isotope values of lacustrine sediment are forced by variation in the position of the circumpolar vortex (CPV) over the Holocene. The CPV defines a cyclonic band of fast moving air over the midlatitudes and at the core of the CPV is the Polar Front Jet Stream. The Polar Front separates cold and dry air to the north from warm and wet air to the south. Therefore, as the distribution of Earth's heat budget changes over time, the shape and latitude of the Polar Front alters, resulting in climate variations sensitive to these changes (Kirby et al., 2002).

We expand this record of atmospheric circulation change across the Atlantic Ocean by developing a high-resolution lacustrine sediment record in western Ireland. Ireland has a temperate maritime climate moderated by proximity to the Atlantic Ocean (Jordan, 1997) and the influence of the Gulf Stream (Kiely et al., 1998) that reduces seasonal variation in temperature and increases temperatures relative to other landmasses at similar latitudes. Ireland is in a particularly sensitive location about which the CPV changes position frequently. The position and shape of the CPV are significant factors in controlling advection of air masses and consequently, moisture to a given region. Decadal-scale climate variation in Western Europe is dominated by the North Atlantic Oscillation (NAO). The NAO not only dominates weather and climate of Western Europe, but also plays a significant role in forcing the weather of North America and Asia (e.g. Hurrell, 1995). Thus, climate records from lake sediment in western Ireland are ideal for reconstruction of circulation mechanisms that affect large regions of the Northern Hemisphere. To this end, we present the first high-resolution oxygen isotope study of a marl lake, Lough Inchiquin, in County Clare western Ireland.

3.3 Background and Study Site

Lough Inchiquin is located in the Burren of County Clare that is unique in its climatological, ecological, and archaeological significance to Ireland (Drew et al., 1994). Bedrock is dominated by nearly pure Lower Carboniferous limestone that was deposited in shallow equatorial seas (Moles, 2002). Many of the lakes in this area generate marl that contains between 60 to 95 wt. % calcite. Several previous climate records have been generated from this region at Lough Gortlecka, Rinn Na Mona, and Lough Goller (Watts, 1985). However, these studies are principally pollen records with age control limited to a few dates. Furthermore, complications with pollen records arise due to variations in the origin (regional or remote) of taxa and timing of vegetation changes lagging behind climate perturbations (Leng and Marshall, 2004).

Lough Inchiquin lies ~20 km to the east of the Atlantic Ocean (Fig. 3.1) and 2 km northwest of the town of Cora Finné. Temperature and dissolved oxygen measurements of this lake indicate that thermal stratification is generally established by June and isothermal conditions return by mid-October (Allott, 1986). Despite strong winds the lake develops a thermocline with a warm epilimnion and a cool hypolimnion (Allott, 1986). Lough Inchiquin covers 110 ha, averages 10.8 m depth and is a maximum of 28 m deep. Clifden Hill (190 m) shelters the lake from prevailing southwesterly winds (Allott, 1986). An Forghas (the River Fergus) drains into Lough Inchiquin from the north and exits to the south. Drew (1988) determined the An Forghas catchment just north of Lough Inchiquin to be 115km^2 based on the flow (3.9 m^{3}s^{-1}) measured from 1984 to 1988 and regional precipitation input (34 Ls^{-1}km^{-2}). The residence time of Lough Inchiquin is ~0.09 yrs (Irvine et al., 2001) making this lake ideal for high-resolution climate studies.

The distribution of stable isotopes in surface waters has previously been examined in Ireland to determine whether individual lakes are appropriate for development of sediment-based paleoclimate records (See Chapter 2). The distribution of surface water isotope values in the Burren is complicated by surface and karstic drainage as well as lakes with variable residence times that display $\delta^{18}O_{lake\ water}$ values ranging between -4.1 and -6.1‰ VSMOW. Hydrologic variables include differences in residence time, catchment size, input of groundwater, and total surface area of the lake (See Chapter 2). In 2002, Lough Inchiquin had a $\delta^{18}O_{lake\ water}$ of -5.9‰VSMOW and a $\delta D_{lake\ water}$ of -37‰ VSMOW, suggesting that evaporation may be lower than other Burren lakes with higher isotope values.

3.4 Methods

A 7.6 m long core (LINC-1) was recovered in June 2002 using a Livingston square-rod piston coring device from the southeastern shoreline of Lough Inchiquin (W09°04’44”, N52°57’03”; Irish Grid number IR: 27750 89570). A second core was retrieved (LINC-2) 2m to the south and was archived. A push core, LINC PC-1, was recovered from the lake ~15m NW of the LINC-1

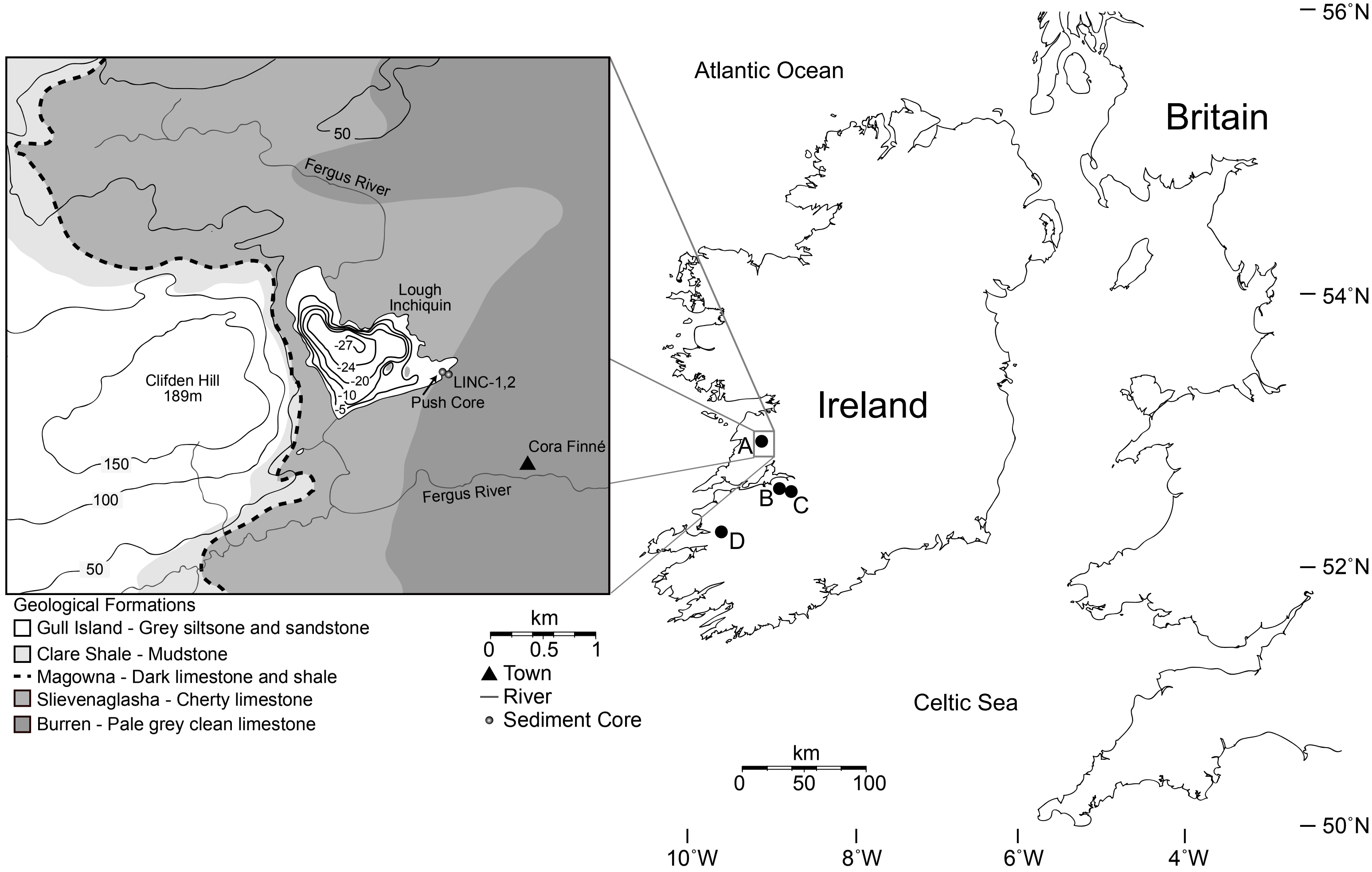

Figure 3.1. Geography of Ireland with location of the study lake, Lough Inchiquin (A) and other sites mentioned in text: Tory Hill (B), Red Bog/Lough Gur (C), and Crag Cave (D). Inset map shows the local surface hydrology, local geology (Geological Survey of Ireland, 1999), and bathymetry of Lough Inchiquin (Allott, N., personal communication, 2004).

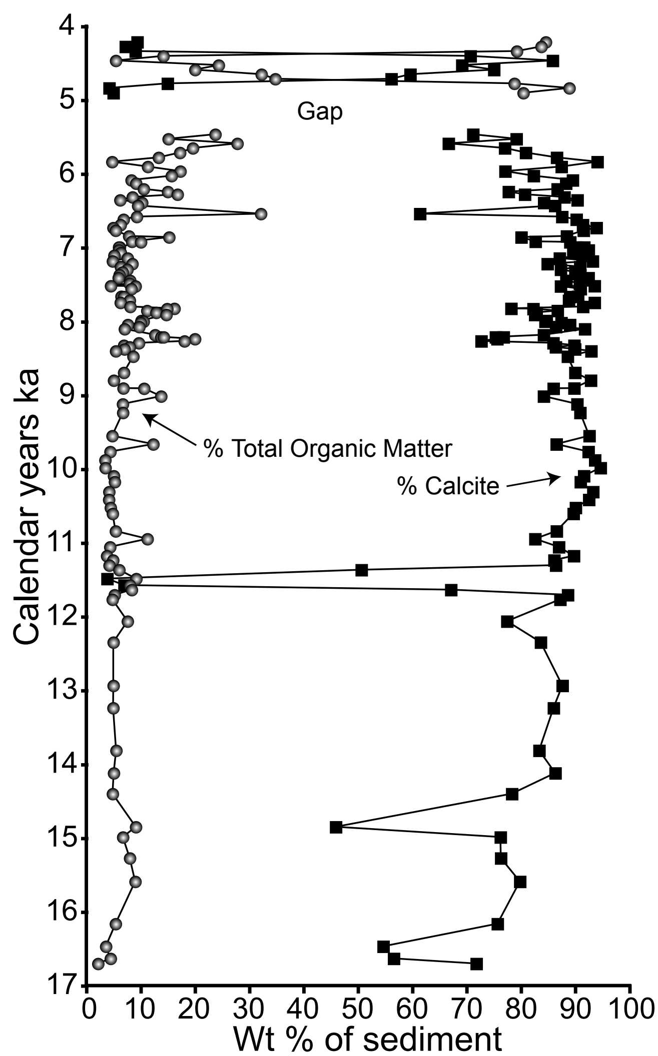

Figure 3.2. TC and TOM revealed by loss on ignition and are with respect to time.

coring site. LINC-1 was opened, split, described, and sub-sampled for loss on ignition (LOI) at the Botany Department, National University of Ireland in Galway and at the Saskatchewan Isotope Laboratory. LOI sampling was conducted at 5 cm spacing for total wt. % organic matter (TOM) and total carbonate (TC; converted to wt. % calcite) by combustion at 550˚C and 1000˚C respectively (Dean, 1974) and are shown in Fig. 3.2 and Appendix B. The gap in LINC-1 is the result of the high compressibility of peat during the coring process as well as a large piece of wood in the core. Differential compressibility of marl, peat, and wood excludes the possibility to realistically remove compression from the 1st meter of sediment.

The core was sliced horizontally into 2 mm segments for ostracod, organic matter, and cellulose isotope analyses. Samples for $\delta^{18}O$ analyses were collected (0.5mm thick) from the base of each 2mm segment (n=3005). Several samples were analyzed to determine mineralogy of the core (Table 3.1) using x-ray diffraction (XRD). Samples from marl rich sections contained calcite with no aragonite or dolomite. Samples from the clay sections were primarily quartz, clay minerals, and some calcite except sample 7.42 m that contains dolomite as well. Local bedrock consists of Visean marine calcite.

Primary age control was established by dating of aquatic macrofossils, bulk calcite, and organics from LINC-1 and LINC PC-1. Samples were dated using AMS ^{14}C at the University of Arizona (Table 3.2, Fig. 3.3). Radiocarbon dates on LINC-1 bulk calcite and macrofossils components are affected by the hard water effect that was quantified by comparing contemporaneous wood and carbonate macrofossils. These samples have a difference of 1575 ^{14}C years which is used to correct LINC-1 macrofossil dates. Macrofossil dates as well as the uppermost organic sample were converted to calendar years before 1950 (cal yr B.P.) using CALIB 4.3 (Stuiver et al., 1998a, b). Our age model (Figure 3.4) is based on linear interpolation between calibrated ages. This age model yields a basal age of 16,750 cal. yr B.P. corresponding to the initial accumulation of late-glacial sediments at Tory Hill (O'Connell et al., 1999). It is possible that the stratigraphically lowest date is offset by a larger hard water effect as $\delta^{13}C_{calcite}$ values at this depth are ~2.5‰VPDB, similar to the bedrock $\delta^{13}C_{calcite}$ of 3.2‰VPDB (See Chapter 4). This suggests that calcite at this depth is derived primarily from Paleozoic bedrock carbon, which is devoid of ^{14}C. Therefore, our age estimate could be up to 1900 years too old based on wiggle matching $\delta^{18}O_{calcite}$ values with the GISP2 $\delta^{18}O_{ice}$ record. This would result in younger ages below 6.7 m and a new basal age of 14,480 cal yr B.P.

Macrofaunal and microfaunal components were separated by stereomicroscope under 30x magnification to limit isotope analyses to fine-grained sediment. $\delta^{18}O$ analyses were conducted in the Saskatchewan Isotope Laboratory at the University of Saskatchewan. Samples were roasted *in-vacuo* at 200˚C for 1 hour to remove volatile organic material and water that may influence isotope values. Samples were analyzed by a Finnigan Kiel-III carbonate preparation device directly coupled

Table 3.1. Mineralogy of core LINC-1

Sample	Sediment type	Mineralogy
2.58	Marl	Calcite
3.50	Marl	Calcite
4.53	Marl	Calcite
5.40	Marl	Calcite
6.51	Clay	Illite/Chlorite and Quartz
6.91	Marl	Calcite
7.22	Clay	Calcite, Dolomite, Illite/Chlorite, and Quartz
7.51	Clay	Calcite, Illite/Chlorite, and Quartz
7.53	Till	Calcite and Quartz
Burren limestone	Limestone	Calcite

Table 3.2. Radiocarbon data for core LINC-1 and LINC PC-1

Core	Depth (m)	Material	^{14}C age (± 1σ)	Lab. Code	Calibrated age (Cal yr B.P.)	$\delta^{13}C$ VPDB
LINC-1						
	0.01	Peat	3959±56	AA54025	4400	-26.8
	1.15-1.20	Organic	7858±67	AA54026	n.a.	-40.7
	1.50	Bulk Calcite	8131±35	AA56893b	n.a.	-6.4
	1.50	Macrofossil	6849±51	AA56893	6090	-9.9
	2.60	Bulk Calcite	8422±34	AA56894b	n.a.	-7.3
	2.60	Macrofossil	6100±170	AA56894	n.a.	-10.2
	3.55	Bulk Calcite	8896±49	AA56889b	n.a.	-7.4
	3.55	Macrofossil	8355±44	AA56889	7635	-9.9
	3.55	Organic	8548±72	AA54027	n.a.	-32.9
	4.90-5.00	Organic	10160±120	AA54028	n.a.	-41.3
	4.97	Bulk Calcite	10081±48	AA56890b	n.a.	-6.1
	4.97	Macrofossil	9000±120	AA56890	8410	-9.5
	6.25	Macrofossil	11383±64	AA56897	11170	-1.4
	6.70	Macrofossil	11777±59	AA56892	11770	-1.2
	7.45	Macrofossil	15039±87	AA56896	16170	2.4
LINC PC-1						
	0.13	Wood	7258±42	AA56891		-28.2
	0.13	Macrofossil	8832±91	AA56898		-10.3

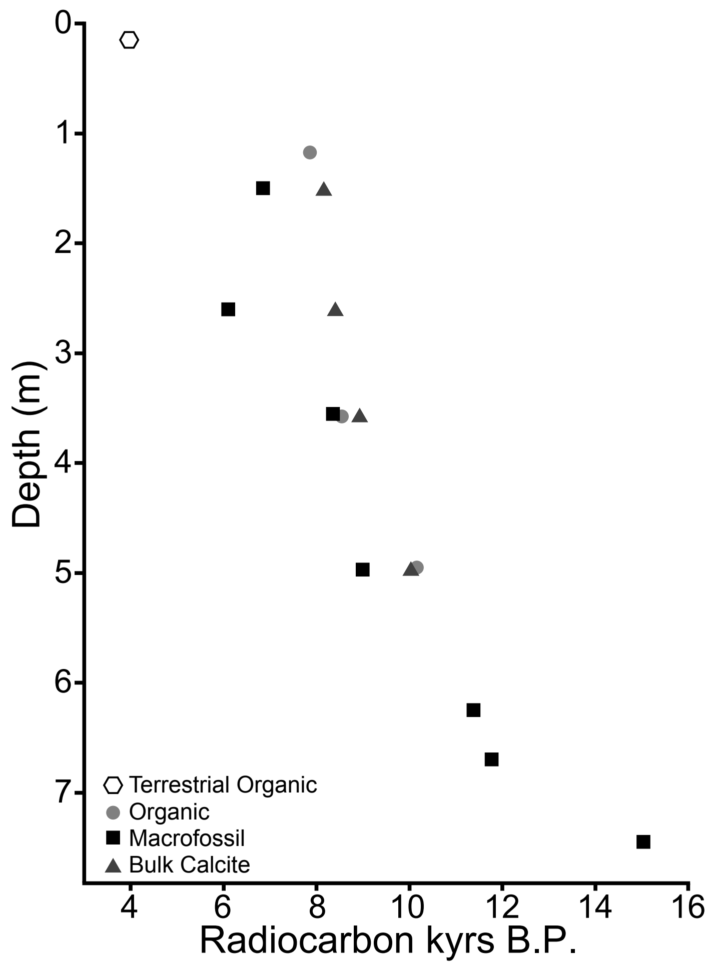

Figure 3.3. Radiocarbon ages for all samples analyzed.

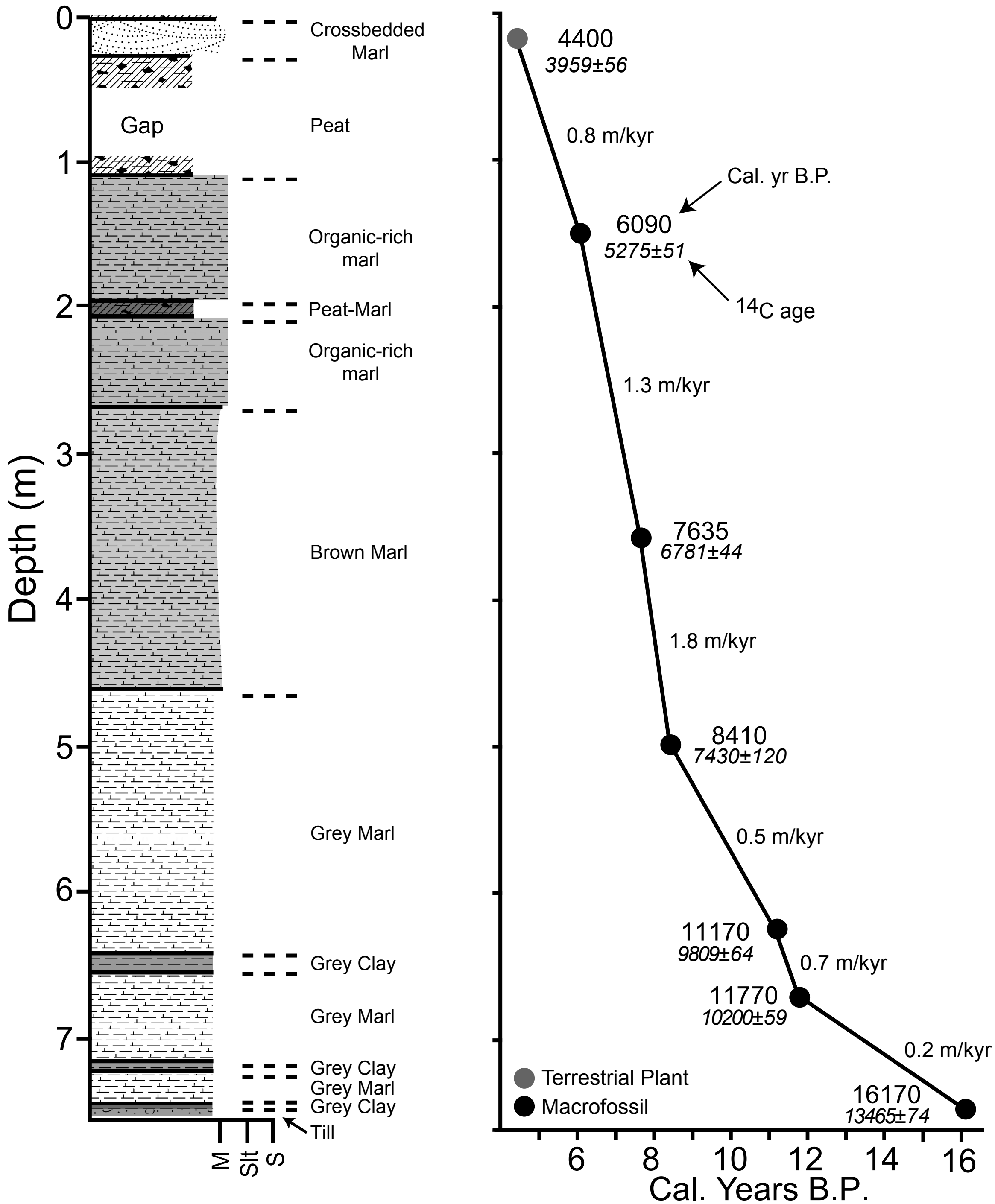

Figure 3.4. Lithology and age model for Lough Inchiquin sediment core based on calibrated radiocarbon ages. Sedimentation rate is based on the accumulation rate in meters per thousand years and is based on the age model.

to a Thermo-Finnigan MAT 253 gas isotope ratio mass spectrometer. Thirty to fifty microgram samples were reacted with 103% anhydrous phosphoric acid for 3 minutes at 70˚C. Samples were corrected for ^{17}O contribution, acid/water fractionation, and temperature fractionation. Values are reported in standard delta per mille (‰) notation relative to the VPDB standard using NBS-19, NBS-18, as well as internal standards. Precision is ±0.16‰ for $\delta^{18}O$ determined on a standard (n=58, 1σ).

3.5 Results

The LINC-1 core is dominantly composed of marl with as much as 94% TC (Figs 3.2 and 3.4). The base of the core displays a gradation between light grey clay and gravel at 7.6 m to dark grey clay at 7.5 m. Partially laminated grey marl begins at 7.5 m and continues to 7.2 m, followed by a thin (<2 cm) grey clay layer. Partially laminated grey marl caps the clay followed by dark grey clay between 6.6 m to 6.4 m. This is overlain by weakly laminated marl that persists to 4.8 m where it transitions to brown non-laminated marl intercalated with weakly laminated marl to 2.1 m. A layer with high peat content from 2.1 m to 2.0 m underlies tan marl with few laminations that persists until 1.25 m. At 1.25 m, highly fossiliferous peat replaces the marl. A gap in the core between 1.00 and 0.5 m is related to the high compressibility of peat during coring. Peat dominates the sediment from 0.5 m and 0.3 m, in turn overlain by an interbedded peat-marl lens 12 cm thick followed by peat to the top of the core.

TC is relatively invariant throughout the core at values >90% with several large anomalies (Fig. 3.2; Appendix B). TC decreases to ~55% at 16,600 cal yr B.P. followed by a rapid increase to 80% by 16,160 cal yr B.P. Another decrease in TC occurs at 15,000 cal yr B.P. The largest excursion in TC begins at 11,700 cal yr B.P. decreasing to ~5% and returning to high values by 11,300 cal yr B.P. Several notable decreases also occur at 9,010, 8,260, 7,820, 6,860, and 6,540 cal yr B.P. Values decrease beginning at 5,840 cal yr B.P. correlated with increasing TOM that may be attributed to changes in the lake level.

$\delta^{18}O_{calcite}$ values in LINC-1 (Fig. 3.5; Appendix C) display significant variability between samples (up to 2.0‰). A rapid ~2‰ increase at the base of the core is followed by lower amplitude variation with a slightly decreasing first order trend to ~10,500 cal yr B.P. A large negative excursion is centered around 11,500 cal yr B.P. where there is a complete loss of TC. A transition from low values to higher values occurs at 10,500 cal yr B.P. This is followed by high frequency, albeit low amplitude, variability with a decreasing asymmetric first order trend to 8,400 cal yr B.P. A transition to more negative values at ~7,500 cal yr B.P. occurs followed by a first order trend towards more positive values.

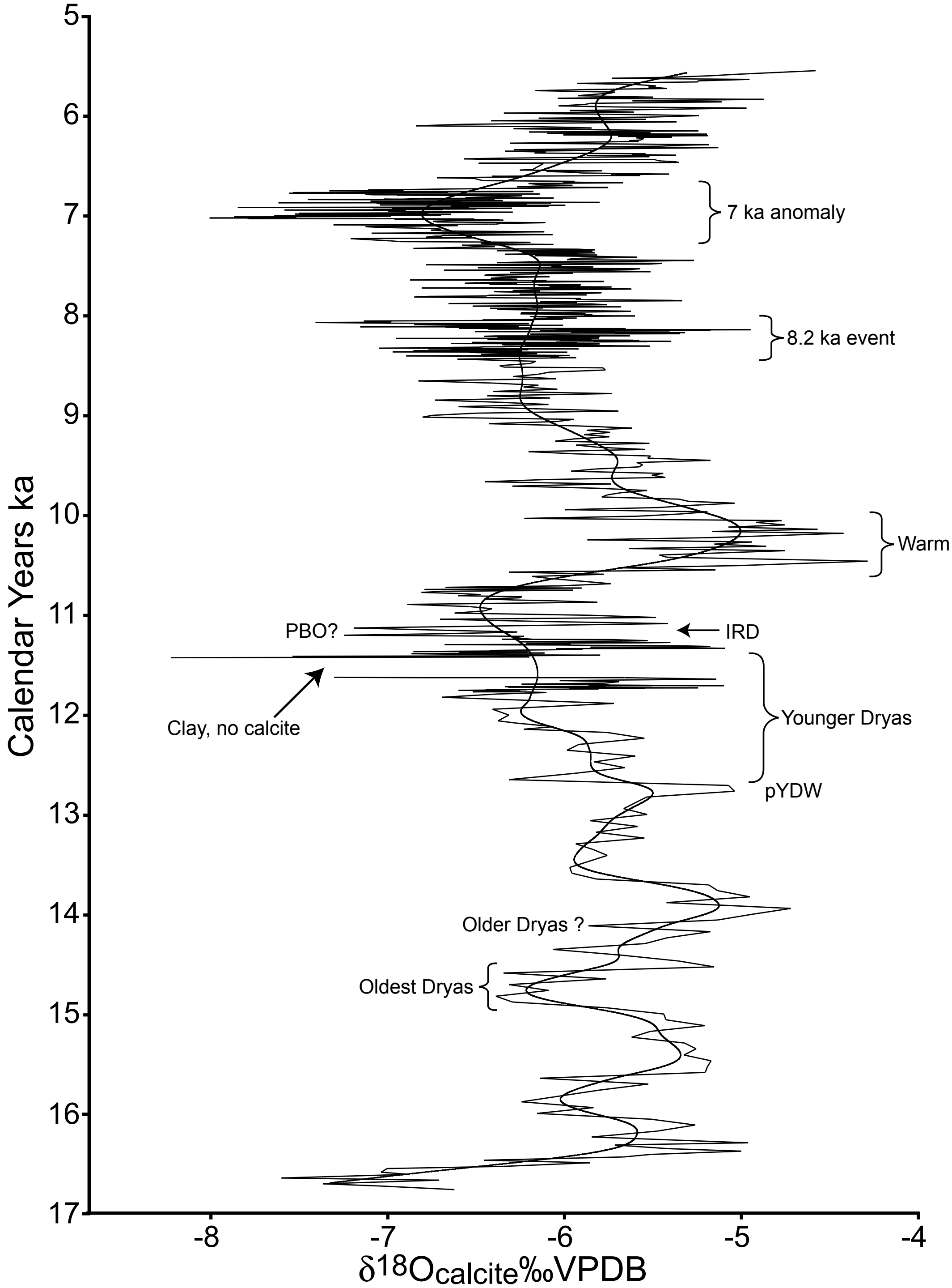

Figure 3.5. $\delta^{18}O_{calcite}$ values vs. age in calendar years before present. Climate anomalies are indicated with brackets and are labeled accordingly. The darker line represents a 50-year spline of $\delta^{18}O_{calcite}$ values that indicates first order trends of long-term shifts in climate. Ice rafted debris from Bond et al. (1997) is labeled as IRD. High values indicate higher temperatures and low values are interpreted as lower temperatures resulting from Rayleigh distillation/atmospheric temperature relationships that force $\delta^{18}O_{precipitation}$ values.

3.6 Discussion

3.6.1 Oxygen Isotopes

$\delta^{18}O_{calcite}$ values of lacustrine sediment are interpreted to reflect changes in water/air temperature and/or $\delta^{18}O_{lake\ water}$. $\delta^{18}O_{lake\ water}$ values vary with changing $\delta^{18}O_{precipitation}$ values that are regulated by condensation temperature, rainout effect, evaporation, relative humidity, and changes in seasonal distribution of precipitation. If we assume that temperature is the primary control, then increasing $\delta^{18}O_{calcite}$ values reflect decreasing lake temperatures. For example, $\delta^{18}O_{calcite}$ values from Lough Inchiquin record high-frequency variability on the order of 2‰ that would translate to ~8˚C (~4˚C/1‰; Kim and O'Neil, 1997) variation in summer temperatures. Because the modern annual temperature range in western Ireland is only 16˚C (MET, 2003), a change of 9˚C in summer temperatures is unrealistic. Therefore, temperature cannot be the only control on variability. Rather, we hypothesize that the predominant control on $\delta^{18}O_{calcite}$ values is variation in $\delta^{18}O_{precipitation}$ values that are forced by changes in atmospheric circulation and air temperature. This approach has been used in multiple lake studies (e.g. Leng and Marshall, 2004). Other researchers in Ireland have reported a positive correlation between $\delta^{18}O_{calcite}$ and air temperature such that $\delta^{18}O_{calcite}/\delta T$ = 0.33‰/˚C (Ahlberg et al., 1996).

3.6.2 Late Glacial Climate Change

The last glacial maximum (Pleniglacial) occurred at ~22,000 cal yr B.P. following Heinrich event 2 and was terminated by rapid deglaciation starting around ~17,400 cal yr B.P. in Ireland and the British Isles (Bowen, 2002). However, the nature and timing of the termination of the Pleniglacial in western Ireland is poorly understood because most climate records (e.g. Watts, 1985) are either inadequately dated or do not extend far enough into the past (O'Connell et al., 1999). At Tory Hill (Site B, Fig. 3.1), Co. Limerick, 53 km south of Lough Inchiquin, a pollen record suggests that at 16,800 cal yr B.P., average temperatures likely did not exceed 5˚C (O'Connell et al., 1999). The termination of the Pleniglacial period was recorded at Lough Inchiquin as characteristic dark grey gravely clays (Watts, 1985) following the disappearance of the Midlandian ice sheet (O'Connell 1999). $\delta^{18}O_{calcite}$ values at the base of the core are –7.6‰ reflecting low $\delta^{18}O_{precipitation}$ values associated with cold atmospheric temperatures and/or snow melt. These low values may be attributed to a detrital calcite component ($\delta^{18}O_{bedrock}$= –10.8‰) mixed with the autochthonous calcite.

The early climate amelioration peaks at 16,300 cal yr B.P., about ~2,300 years earlier than the GISP2 core (Fig. 3.6; Stuiver et al., 1995). We attribute the warming to a northerly advance of the Gulf Stream. However, climate was not stable as $\delta^{18}O_{calcite}$ values decrease from 16,400 to 15,600 cal yr B.P. followed by another amelioration.

The Oldest Dryas period is recognized at Lough Inchiquin as a distinctive decrease in TC. The timing of the onset of this event is similar to that observed in Greenland ice core data at 15,100

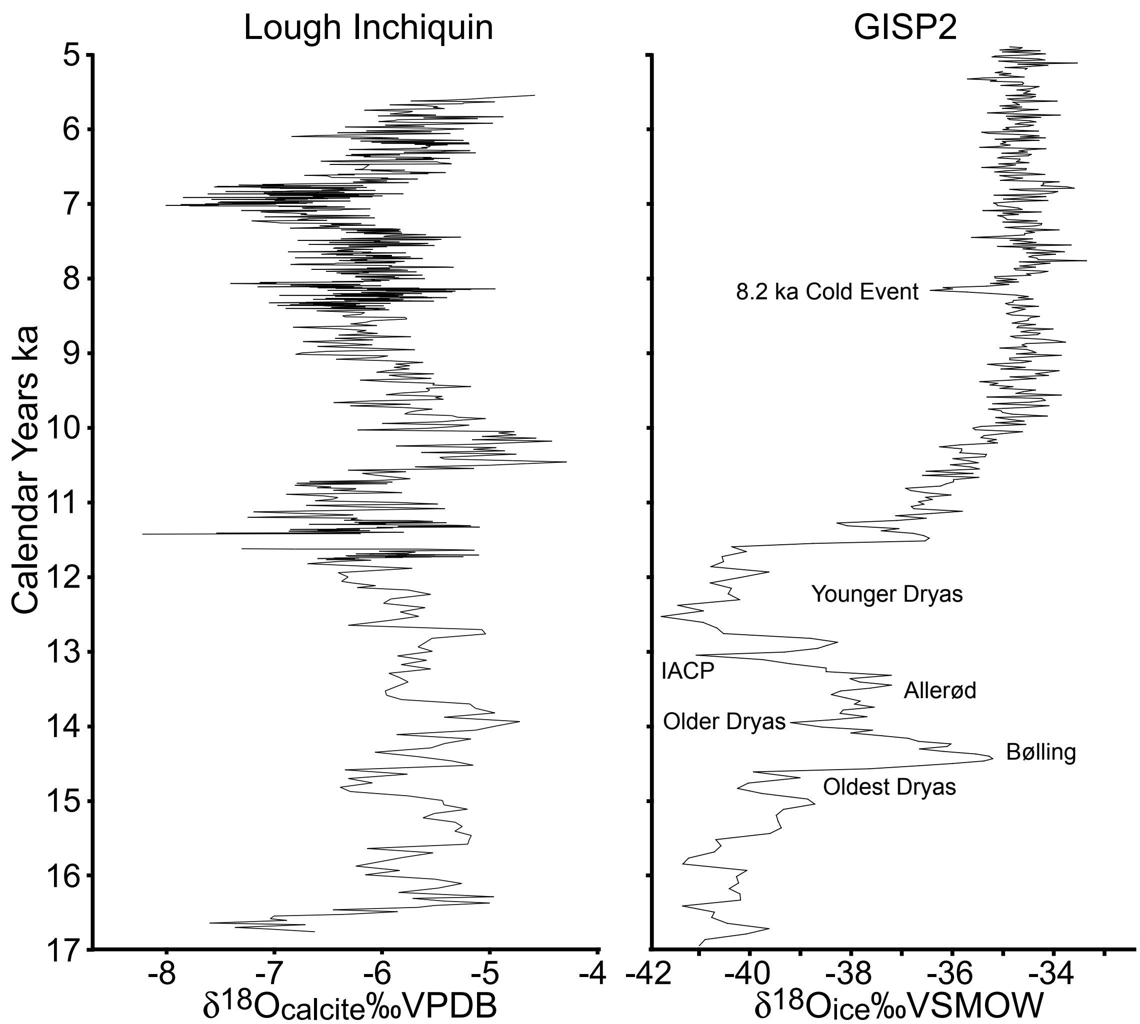

Figure 3.6. Comparison of $\delta^{18}O_{calcite}$ values at Lough Inchiquin to $\delta^{18}O_{ice}$ values of the GISP2 ice core record and associated climate events (Stuiver et al., 1995). Cold/cool periods are indicated by low $\delta^{18}O_{ice}$ and warm periods are indicated by high $\delta^{18}O_{ice}$.

cal yr B.P. but lasts ~200 years longer. The climate anomaly at this time is also apparent in the $\delta^{18}O_{calcite}$ record as a ~1‰ decrease in values suggesting a decrease in temperature. Increased TC and $\delta^{18}O_{calcite}$ values by ~14,600 cal yr B.P. suggest warming characteristic of the Bølling period. Proxy records suggest that the Bølling was as warm as today (e.g O'Connell et al., 1999). Fluctuations in $\delta^{18}O_{calcite}$ values suggest that this period was unstable and it is possible that the excursion at ~14,100 cal yr B.P. is the Older Dryas event that is identified in Greenland (Stuiver et al., 1995).

Highest $\delta^{18}O_{calcite}$ values during the Late Glacial occur between 14,100 and 13,900 cal yr B.P., suggesting that this may have been the warmest period of the late Glacial. $\delta^{18}O_{calcite}$ values and a chironomid record from Hawes Water in northwest England suggest a regional warming at 14,100 GRIP yr (Jones et al., 2002). $\delta^{18}O_{calcite}$ values suggest that temperatures increased until 13,700 cal yr B.P. as a rapid decrease in $\delta^{18}O_{calcite}$ occurs. $\delta^{18}O_{ice}$ values suggest the Allerød period in Greenland (14,000-12,900 cal yr B.P.) is characterized by lower temperatures than the Bølling period (Stuiver et al., 1995). However, our record shows higher values early in the Allerød compared to the Bølling.

The rapid decrease at 13,700 cal yr B.P. may reflect the intra-Allerød cold period (IACP), however the timing of these events is poorly constrained. The period between 13,700 and 13,570 cal yr B.P. may represent the IACP identified by Lehman and Keigwin (1992). In context with other regional records, Hawes Water in northwest England (Marshall et al., 2002), and Lough Inchiquin display a similar series of events in $\delta^{18}O_{calcite}$ from 13,900 to 13,750 GRIP yr.

Following the end of the Allerød, a warming period is suggested by an increase in $\delta^{18}O_{calcite}$ at 12,750 cal yr B.P. O'Connell et al. (1999) report evidence for a regional warming of unknown magnitude. This period was informally deemed the pre-Younger Dryas Warming (pYDW) by O'Connell et al. (1999). Our $\delta^{18}O_{calcite}$ values for the pYDW are nearly as high as those of the early Allerød and correlative with a record from Lough Gur, Red Bog (Ahlberg et al., 1996) and at Tory Hill (O'Connell et al., 1999). Lehman and Keigwin (1992) suggest that this period represents a short lived increase in North Atlantic sea surface temperatures at 11,300 ^{14}C yr B.P. Increasing temperatures documented by marine molluscs indicate increased equatorial heat transport facilitated by North Atlantic surface circulation (Peacock, 1989) thereby explaining the increase in $\delta^{18}O_{calcite}$ values in western Ireland.

The Younger Dryas (YD) is manifested in our record as a decrease from the high pYDW $\delta^{18}O_{calcite}$ values as well as a small (<10%) decrease in TC. The YD is documented by multiple proxies in records across Europe and North America (e.g. Alley et al., 1993; Jones et al., 2002). The YD resulted from shutdown of the Atlantic oceanic conveyor-belt by meltwater pulses. This led to a decrease in surface water salinity and density where North Atlantic Deep Water forms (Broecker et al., 1989). The North Atlantic oceanic conveyor belt transports enormous amounts of heat to the atmosphere at mid and high latitudes (Broecker et al., 1985). During the YD, there was a readvance of polar waters in the North Atlantic as far south as 53˚N (Ruddiman et al., 1977), while summer sea surface temperatures derived from foraminifera record ocean temperatures decreasing by 10˚C off the coast of Ireland (Duplessy et al., 1996).

The onset of the YD is characterized by a large decrease in $\delta^{18}O_{calcite}$ values punctuated by several increases that indicate the onset of the YD was a stepwise process (Alley, 2000). TC values record a slight decrease at this time. O'Connell et al. (1999) characterized the early YD as a period of high winter precipitation that may be masked by detrital carbonates supplied by increased solifluxion. However, we believe that a detrital signal is unlikely because the limestone bedrock is Visean (Carboniferous) with $\delta^{18}O_{calcite}$ values between ~–3 to –8‰ (Bruckschen et al., 1999) and we determined bedrock $\delta^{18}O_{calcite}$ values at Lough Inchiquin to be –11.4‰. It is likely that higher $\delta^{18}O_{calcite}$ values in the early part of the YD reflect a regional climate signal and Ahlberg et al. (2001) suggested this may be accounted for by dominantly Westerly winds during this time generating higher $\delta^{18}O_{calcite}$ values from oceanic derived precipitation.

Our YD data is similar to the GISP2 data in that $\delta^{18}O$ values are lower than the Bølling and Allerød periods. However, Lough Inchiquin displays continually decreasing values. The largest anomaly in our record occurs at 11,750 cal yr B.P. with a significant increase in values just prior to the largest decrease in TC. The most severe climate deterioration in Ireland during the YD appears much later than other records and was noted by O'Connell et al. (1999) as well. Elevated $\delta^{18}O_{calcite}$ values prior to and just after the clay layer in our record may be evidence for increased evaporation (evaporation of lake water results in higher $\delta^{18}O_{lake\ water}$) as a result of increased winds. Perturbations in atmospheric circulation at this time have been previously suggested from dune formations in Europe as a result of high westerly winds during the YD (Isarin et al., 1997). Further evidence for climatic instability from 11,800 to 11,500 cal yr B.P. may be explained by persistent changes in the position of the oceanic front separating sea ice covered water from relatively warm water (Ebbesen and Hald, 2004).

3.6.3 The Holocene

Following the end of the YD in the GISP2 record (11,600 cal yr B.P.), $\delta^{18}O_{calcite}$ values at Lough Inchiquin increase rapidly (~3‰) suggesting climate amelioration. However, this amelioration is brief and followed by a rapid decrease in $\delta^{18}O_{calcite}$ values. This depression in climate following renewed warmth has not been previously recognized in Ireland. High frequency variability following the YD is likely associated with changes in meltwater supply to the North Atlantic that forced changes in oceanic and atmospheric circulation (Andrews et al., 1991). Beginning in 11,335 cal yr B.P., the PreBoreal Oscillation caused by melt water pulses from Lake Agassiz that persisted until 10,750 cal yr B.P. (Fisher et al., 2002) likely influenced rapid changes in $\delta^{18}O_{calcite}$ values at Lough Inchiquin. The PreBoreal Oscillation led to increases in pack ice on the North Atlantic

Ocean that decreased surface temperatures, increased albedo, and likely forced changes in ocean circulation (Fisher et al., 2002). Ice rafted debris (IRD) in the form of hematite stained grains and Icelandic glass in an oceanic core recovered near western Ireland indicates that sea ice may have reached as far south as the Irish coast (Bond et al., 1997; Fisher et al., 2002). IRD is dated to 11,100 cal yrs B.P. coeval with an increase of $\delta^{18}O$ in benthic foraminifera that persists for several hundred years (Fig. 3.2 in Bond et al., 1997) again suggesting a decrease in sea surface temperatures. The position of the pack ice likely affected ocean circulation by pushing the equatorial heat supply to the east. This resulted in the polar front advancing southward with the development of pack ice that further decreased atmospheric temperatures, resulting in a period of lower $\delta^{18}O_{calctie}$ values after the YD. An asymmetric increase towards 10,800 cal yr B.P. is similar to events recorded by Lake Ontario sediment (McFadden et al., 2004).

A stepwise increase in $\delta^{18}O_{calcite}$ that begins at ~10,800 cal yr B.P. is not present in the Greenland ice records (Stuiver et al., 1995). As there are no apparent changes in TC and TOM, it is likely that this increase results from changes in the Polar Front related to the decrease of the pack ice. As the Polar Front moved to more northerly latitudes, a rapid increase in atmospheric temperature resulted in higher $\delta^{18}O_{precipitation}$ values. Maximum $\delta^{18}O_{calcite}$ values are reached at this time suggesting that this was the warmest period in our record and signify the end of Late Glacial type environments in Ireland.

High frequency, low amplitude variation, around 8,200 cal yr B.P. is likely related to the "8.2 ka cold event" (8.4 to 8.0 ka) identified in Greenland ice cores (Alley et al., 1997) and elsewhere in Europe (e.g. McDermott et al., 2001; Magny and Bégeot, 2004). An increase in TOM and a decrease in TC suggest that cooling was initiated at 8,400 cal yr B.P. These events are correlative with the catastrophic drainage of Lake Agassiz through Hudson's Bay at 8,400 cal yr B.P. (Barber et al., 1999; Teller et al., 2002) that resulted in cold, dry, and windy conditions adjacent to the North Atlantic (Alley et al., 1997). This event is observed in multiple climate proxies across Europe (e.g. McDermott et al., 2001; Magny and Bégeot, 2004; Veski et al., 2004) and North America (McFadden et al., 2004). Increasing $\delta^{18}O_{calcite}$ values at 8,100 cal yr B.P. and high frequency variation suggest initiation of warming. High frequency variation may be explained by rapid changes in the latitudinal and longitudinal position of the polar front. Magny and Bégeot (2004) found evidence for a perturbation in atmospheric circulation (e.g. Alley et al., 1997; Renssen et al., 2001; Tinner and Lotter, 2001) that suggests a southerly displacement of the Polar Front as well as changes in the position of cyclone tracks in Western Europe (Renssen et al., 2001). The 8,200 cal yr B.P. event in our record is not as prominent as is observed in other records (Stuiver et al., 1995; McDermott et al., 1999). However, the climate signal from a speleothem at Crag Cave in western Ireland (D, Fig. 3.1) indicates decreased precipitation, plant coverage, and temperatures as well as increased hydrological residence times (McDermott et al., 1999, Baldini et al., 2002). These environmental conditions would decrease the supply of precipitation with low $\delta^{18}O$ values. Therefore, higher $\delta^{18}O_{calcite}$ values predominantly reflect low lake water temperatures.

At ~7,300 cal yr B.P. the largest perturbation in Holocene climate at Lough Inchiquin is observed as a negative excursion in $\delta^{18}O_{calcite}$ that persists until ~6,700 cal yr B.P. This anomaly has not been documented, to our knowledge, elsewhere in Ireland or in the GISP2 record. However, a similar climate excursion is present in a North American sediment record from Lake Ontario (McFadden et al., 2004). Because TC and TOM are not affected during this time perhaps temperatures did not change considerably. Therefore, this period of low $\delta^{18}O_{calcite}$ values likely represents a period of increased winter precipitation (low $\delta^{18}O_{precipitation}$ values) that would decrease $\delta^{18}O_{lake\ water}$ values. High lake levels between 7550 to 7250 cal yr B.P. (Magny and Bégeot, 2004) are in agreement with our interpretation of isotope data in suggesting an increase in precipitation.

3.7 Conclusion

$\delta^{18}O_{calcite}$ values and LOI data recovered from a core at Lough Inchiquin provide a continuous archive of western Ireland paleoclimate between 16,800 and 5,500 cal yr B.P. Ireland is particularly sensitive to climate variability because it is located in the eastern Atlantic Ocean where minor changes in thermohaline circulation, oceanic circulation, atmospheric circulation, and the NAO have a significant effect on the $\delta^{18}O_{precipitation}$ and therefore the $\delta^{18}O_{calcite}$ values. $\delta^{18}O_{calcite}$ values provide proxy evidence for changes in these variables. Based on this information, the climate of Ireland was highly variable through the Late Glacial and early to mid Holocene. Several previously unidentified climate anomalies in western Ireland were identified in our study at 10,800 and 7,100 cal yr B.P. Following the Younger Dryas event, $\delta^{18}O_{calcite}$ values recover strongly, followed by decreasing values and then show an asymmetric increase in values similar to events recorded by Lake Ontario (McFadden et al., 2004). Increased winter precipitation between 7,300 and 6,700 cal yr B.P. is likely responsible for the significant decrease in $\delta^{18}O_{calcite}$ values. This is the first high-resolution climate record for western Ireland that extends back to 16,800 cal yr B.P. and provides evidence for rapid climate change in western Ireland during the Late Glacial and the early Holocene.

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3.10 Manuscript's Relationship to the Thesis

Chapter 3 presents a record of $\delta^{18}O_{calcite}$ variability through the Late Glacial and early Holocene at Lough Inchiquin in western Ireland. This chapter is directly related to the thesis as this chapter provides evidence for climate variability in western Ireland and relates the Irish record to a bigger picture circulation model.

CHAPTER 4. CLIMATE CHANGE AND LANDSCAPE EVOLUTION FROM 16,500 TO 5,300 CALENDAR YEARS BEFORE PRESENT AT LOUGH INCHIQUIN, WESTERN IRELAND INFERRED FROM A MULTIPROXY STUDY OF LAKE SEDIMENTS

4.1 Abstract

In order to evaluate secular trends in climatic variability and landscape evolution in western Ireland, we recovered a 7.6 m sediment core that provides proxy evidence. Carbon isotope values of calcite and bulk organic material were determined along with total organic carbon, total nitrogen, C/N ratios, total organic matter, and total calcite on sediment from Lough Inchiquin. We observe significant (~12‰) variations in carbon isotope values of calcite and bulk organics from the Late Glacial to the Holocene at Lough Inchiquin that record temporal shifts in the relative contributions of carbon from limestone weathering versus the supply of terrestrial organic matter. Variations in carbon isotope values are quasi-synchronous with changes in regional vegetation documented by pollen studies. We propose that terrestrial vegetation increased at the end of the Pleistocene due to climate amelioration that resulted concomitant with soil development. The decrease in $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ at Lough Inchiquin is forced by decreasing $\delta^{13}C_{DIC}$ values that result from greater input of soil carbon relative to carbon weathered from limestone. During extreme climate perturbations such as the Older Dryas and the Younger Dryas, an increase in $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values is indicative of decrease in the soil carbon flux. Comparison of $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values reveals that variations in terrestrial particulate organic carbon varies through time and reaches a maximum flux at ~9 ka in response to woodland development beginning at ~10 ka. Quantification of exogenous fluxes of carbon into lake systems is critical for the proper interpretation of lacustrine $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values.

4.2 Introduction

Lake studies that employ carbon isotope values are generally limited to the analysis of biotic and abiotic calcite (e.g. Talbot, 1990; Kirby et al., 2002; Leng and Marshall, 2004). However, some studies also analyze bulk organic matter (e.g. Schleske and Hodell, 1991; 1995; Meyers and Horie, 1993), sediment cellulose (e.g. Beuning et al., 1997; Wolfe et al., 1997; 2001) and specific compounds (Filley et al., 2001). Climate records based on carbon isotope values from multiple proxies better characterize paleoclimate and the paleoenvironment than single proxy studies. Studies of organic matter in small lakes have shown that inputs of terrestrial organic carbon are difficult to quantify and, thus, complicate the interpretation of climate variability from organic matter carbon isotope values (Pace et al., 2004; Lücke et al., 2003). $\delta^{13}C$ values in freshwater lakes are primarily attributed to reflect changes in the $\delta^{13}C$ values of the Dissolved Inorganic Carbon (DIC) (Hammarlund et al., 1997; Kelts and Hsü, 1978). However, DIC in turn is influenced by mixing of groundwater, surface water, bedrock, and catchment soils (Leng and Marshall, 2004). Carbon isotopes can be used to derive information related to photosynthesis, productivity (e.g., McKenzie, 1985), nutrient availability (e.g., Hollander and Smith, 2001), precipitation and cloud cover (Kirby et al., 2002), as well as paleoecological changes (e.g., Wolfe et al., 1999). Carbon isotopes are also used to reveal tree line retreat (Wolfe et al., 1999) and floral landscape evolution (Hammarlund et al., 1997), which are important consequences of global climate change.

This study focuses on the elucidation of environmental changes at Lough Inchiquin and the surrounding area during the Late Glacial and Holocene by the employment of $\delta^{13}C$ values of sedimentary organic matter and calcite. Landscape evolution and climate variability will be interpreted from the evaluation of $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values. Changes in the flux of terrestrial particulate organic matter will be determined by differences between $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values ($\Delta\delta^{13}C_{calcite - org}$) as an additional proxy for landscape evolution.

4.3 Background

4.3.1 Study Site

The Burren of County Clare, western Ireland (Fig. 4.1) is predominantly characterized by a thick stratigraphy of Carboniferous karstic limestone. Over the past ~2 ka, the upland regions were dominated by exposed limestone with little vegetation. Most areas of The Burren are covered by a thin veneer (several cm) of soil except in lowlands and valleys that are blanketed by significantly more vegetation and soil (Watts, 1984). The soils of The Burren are predominately rendzinas (~90%) with 35% organic content, a pH below 7, and low carbonate contents (Drew, 1983). The bare limestone is characterized by surfaces with deep fissures following joint and bedding planes that provide habitats for herbs, ferns, and mosses (Dickinson et al., 1964). Figure 4.2a emphasizes the nearly unvegetated nature of the limestone bedrock and the landscape around Lough Inchiquin was likely similar during the late Pleistocene. Lough Inchiquin is situated ~20 km to the east of the Atlantic Ocean (Fig. 4.1) and 2 km northwest of the town of Cora Finné. Temperature and dissolved oxygen measurements at Lough Inchiquin (Fig. 4.2b) indicate that thermal stratification is established by June with a warm epilimnion and a cool hypolimnion despite strong winds (Allott, 1986). By mid-October, isothermal conditions return (Allott, 1986). Lough Inchiquin covers 110 ha with an average depth of 10.8 m. Clifden Hill (Fig. 4.1) shelters the lake from prevailing southwesterly winds (Allott, 1986). The main inlet and outlet of Lough Inchiquin is the Fergus River entering from

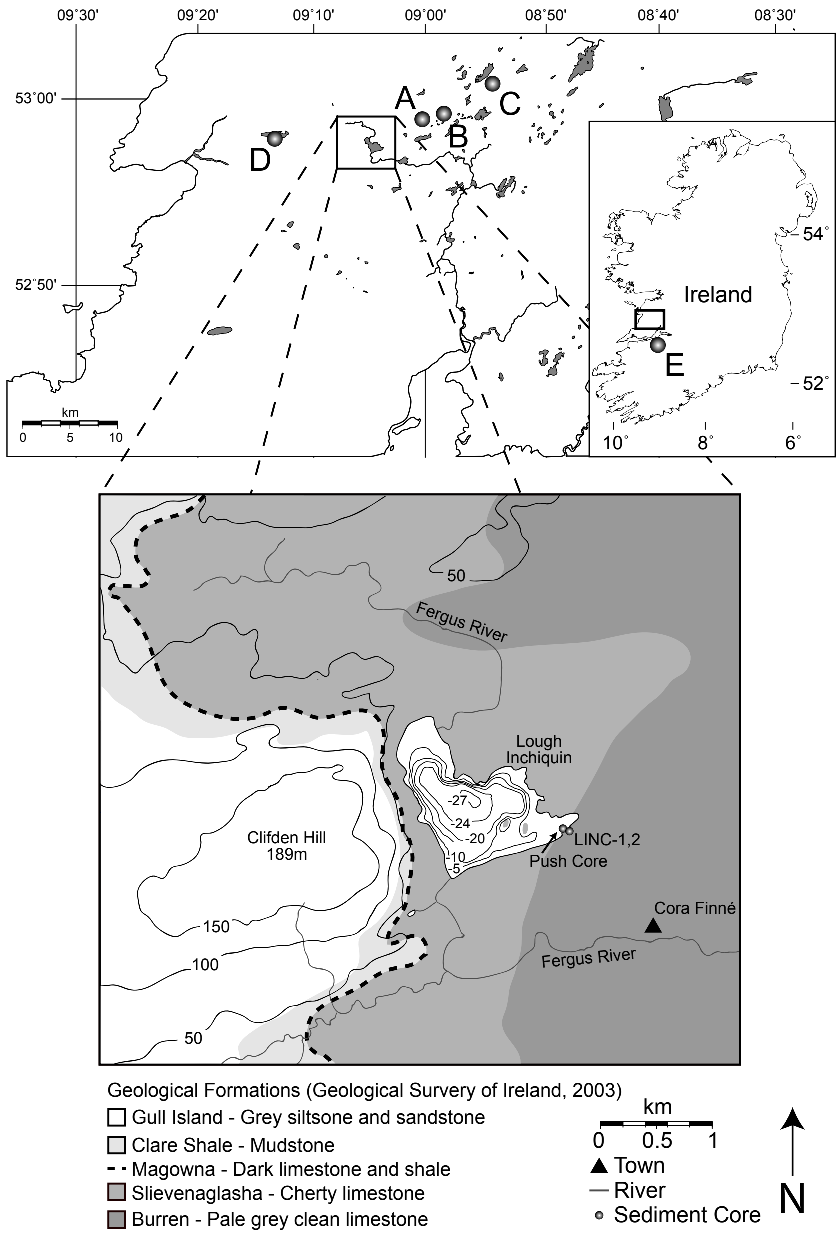

Figure 4.1. Map of Ireland, study area, and detailed map of Lough Inchiquin including geology and bathymetry (N. Allott, 2004, personal communication). Sites of interest mentioned in text: A = Rinn na Mona; B = Lough Gortlecka; C = Poulroe; D = Lough Goller; E = Tory Hill.

Figure 4.2. The upper photo (A) shows Lough Gallaun (near Lough Gortlecka) with Mullaghmore in the background. Vegetation around Lough Inchiquin was likely similar during the late Pleistocene and Early Holocene. The lower photo (B) is of Lough Inchiquin looking to the southeast.

the north and exiting from the south. Drew (1988) determined the Fergus River catchment just north of Lough Inchiquin to be 115km^2 based on the flow (3.9 m^3s^{-1}), measured from 1984 to 1988, and regional precipitation input (34 $Ls^{-1}km^{-2}$). The residence time of Lough Inchiquin is short, ~0.09 yrs (Irvine et al., 2001), making this lake ideal for high-resolution climate studies.

4.3.2 Vegetation History

The vegetation history during the Late Glacial and Holocene at Lough Inchiquin has not yet been evaluated by pollen to our knowledge. However, several adjacent sites in western Ireland, including The Burren, have been studied previously (Fig. 4.1). The closest sites, Lough Gortlecka and Lough Goller, provide vegetation histories of the Late Glacial period. During the Late Glacial, the flora of the surrounding landscape was primary composed of herbaceous plants (*Cyperaceae*) and grasses (such as *Gramineae*) with only minor amounts of birch (*Betula*) (Watts, 1963). Similar floral communities are observed elsewhere at Poulroe 13 km to the northeast (Watts, 1984) and Tory Hill 53 km to the south (O'Connell et al., 1999). Mugwort (*Artemisia*) as well as algal components were present at Tory Hill between 16.8 and 15.0 ka. Temperature estimates from pollen analyses suggest that the Late Glacial temperatures were likely -20˚C during the winter and likely did not exceed 5˚C during the warmest summer months (O'Connell et al., 1999). The deposition of clay and silt at Tory Hill indicates unstable soils at 15.0 ka (O'Connell et al., 1999) indicating the severity of the Oldest Dryas environmental perturbation. This indicates that vegetation was poorly developed if present at all prior to the Younger Dryas (YD) in The Burren.

Younger Dryas vegetation (12.8 to 11.5 ka; Stuiver et al., 1995) is characterized primarily by *Artemisia*, *Cyperaceae*, and *Rumex* (sorel) at all sites. Clay-rich layers in the sediment profile record a period of soil erosion (Watts, 1963; 1984; O'Connell et al., 1999) and/or aeolian deposition (Isarin et al., 1997). Shortly after the YD, vegetation was primarily herbaceous with increasing amounts of grass (Watts, 1963; 1984; O'Connell et al., 1999), followed by a transition to pioneer vegetation consisting of shrubs and herbs at Gortlecka and Rinn na Mona (Watts, 1984). *Betula* was replaced with *Pinus sylvestris* (pine; macrofossil evidence) and *Corylus* (hazel), subsequently replaced by *Ulmus* (elm) and *Quercus* (oak). The establishment of pine in The Burren may have been the earliest (~10,000 cal. yr B.P.) recorded in western Ireland (Watts, 1984). In spite of the presence of woodland at this time, there was still open ground in places indicated by *Calluna* (heather) and *Pteridum* (grasses). A pastoral based human culture arrived in The Burren during the Neolithic (c. 4000 B.P.), which resulted in grazing (Herity and Eogan, 1977; Watts, 1984). However, despite grazing, there is no evidence of soils in the lake sediments at Gortlecka or Rinn na Mona (Watts, 1984). Drew (1983) proposes the soil was likely lost during the latter parts of the Bronze Age, which is subsequent to our sediment record.

4.4 Methods

4.4.1 Sample Collection

A 7.6 m square-rod piston core (LINC-1) was retrieved from the edge of Lough Inchiquin (W09˚04’44”, N52˚57’03”; Irish Grid number IR: 278 896) in July 2002. A push core (LINC PC-1) was retrieved in the lake during July 2003 in 1 m of water approximately ~15 m to the northeast of LINC-1 (Fig. 4.1). Loss on ignition (LOI) sampling (Fig. 4.3) was conducted at 5 cm spacing for wt. % Total Organic Matter (TOM) and wt. % Total Calcite (TC; wt. % carbonate converted to wt. % calcite) by combustion at 550˚C and 1000˚C respectively (Dean, 1974). The core was sliced horizontally into 2-mm segments for bulk organic studies. Samples for $\delta^{13}C_{calcite}$ analysis were collected (0.5mm thick) from the stratigraphically lower portion of the 2 mm segments (n=3005). The primary mineralogy of the core (from XRD) is calcite with clay predominantly in three distinct layers (Fig. 4.3) characterized by illite, chlorite and quartz.

4.4.2 Bulk Calcite Sediment Analysis

$\delta^{13}C_{calcite}$ analyses were performed on fine-grained sediment by removal of macrofaunal and microfaunal components. Samples were roasted *in-vacuo* at 200˚C for 1 hour to remove volatile organics and water. Samples were analyzed in the Saskatchewan Isotope Laboratory at the University of Saskatchewan using a Thermo-Finnigan Kiel-III carbonate preparation device directly coupled to a Thermo-Finnigan MAT 253 gas isotope ratio mass spectrometer. Thirty to fifty μg samples were reacted with 103% anhydrous phosphoric acid for 3 minutes at 70˚C. Samples were corrected for ^{17}O contribution and the acid/water fractionation. Values are reported in standard delta permil (‰) notation relative to the VPDB standard using NBS-19 and NBS-18. Reproducibility of $\delta^{13}C_{calcite}$ is ±0.05‰ based on repeated measurement of a sample (n=58, 1σ).

4.4.3 Bulk Organic Sediment Analysis

$\delta^{13}C_{org}$ were performed on the bulk sediment. Samples were sieved (<500 μm) to remove larger terrestrial derived material (Wolfe et al., 2001). Calcite was removed from samples by acidification with 10% HCl in 50 mL centrifuge tubes for not more than 3 hrs. Samples were then centrifuged, supernatant decanted, and washed with deionized water to remove the HCl. The air-dried samples were dried *in-vacuo* at 40˚C for 2 hours to remove any moisture. Prior to isotope analyses, samples were homogenized using a mortar and pestle. Examples of modern terrestrial organic matter were collected from living plants around the lake. Samples were washed with deionized water and dried *in-vacuo* 40˚C for two hours. $\delta^{13}C_{org}$ analyses, as well as Total Organic Carbon (TOC) and Total Nitrogen (TN), were determined via continuous flow using a Thermo Finnigan Flash Elemental Analyzer by oxidation at 1000˚C followed by reduction to CO_2 and N_2 at 680˚C. CO_2 and N_2 were subsequently passed through a 5Å molecular sieve gas chromatograph at

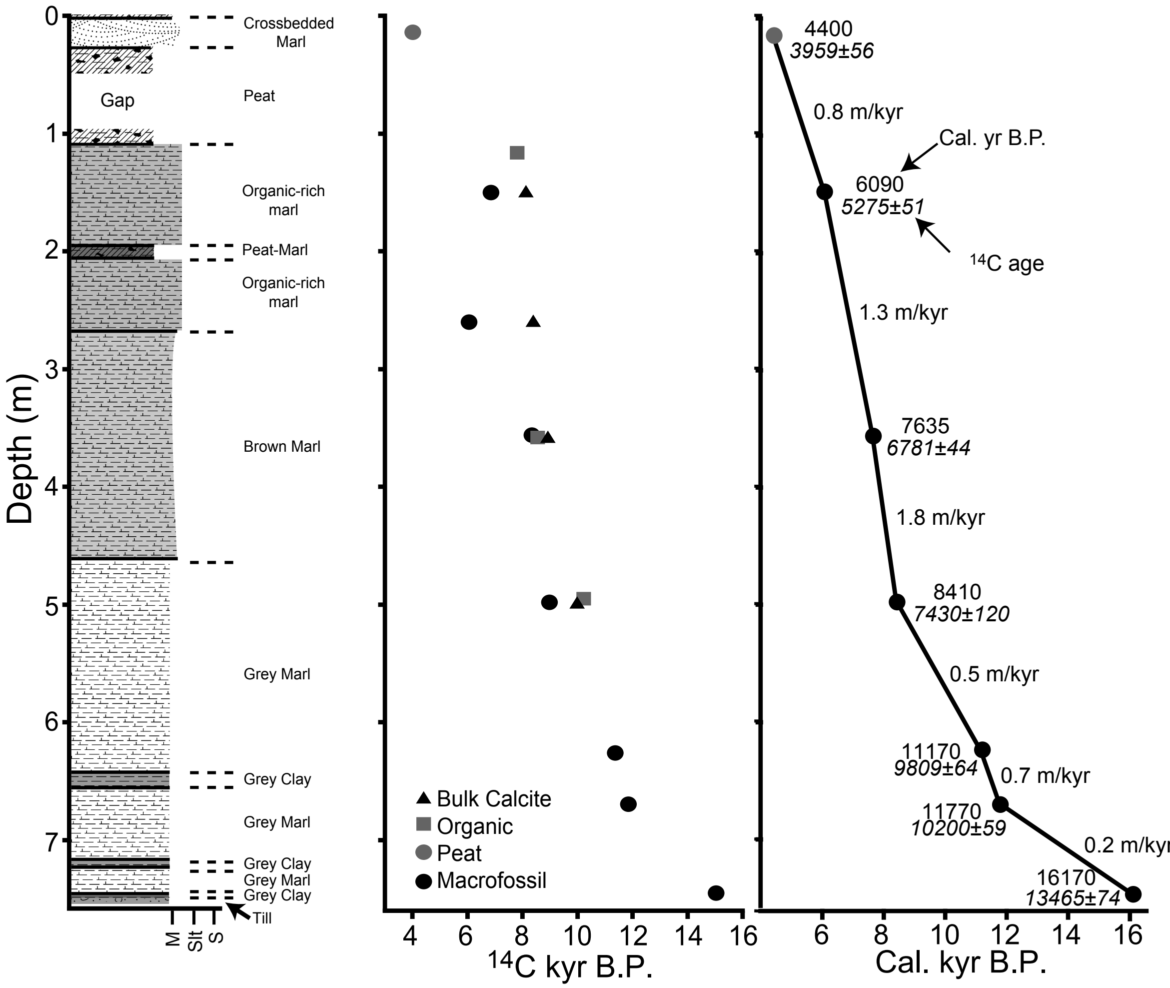

Figure 4.3. Lithology, all radiocarbon ages, and age model for Lough Inchiquin sediment core. Age model is based linear interpolation between calibrated radiocarbon ages that have been corrected for a reservoir effect.

50°C and a Conflo III interface/open split for helium dilution of CO_2. CO_2 and N_2 were measured on a Thermo Finnigan MAT Delta Plus XL mass spectrometer relative to reference gases. $\delta^{13}C$ values were normalized to the VPDB scale using a two-point calibration with well-defined internal standards. $\delta^{13}C_{org}$ is corrected for ^{17}O contribution. Reproducibility of $\delta^{13}C_{org}$ is ±0.1‰ (n=45, 1σ) based on repeated measurements of a sample. TOC and TN were corrected using the acid insoluble fraction and the reproducibility of TOC and TN is ±0.6% (n=6, 1σ) and ±0.07% (n=6, 1σ) respectively. Carbon/Nitrogen (C/N) ratios were determined from the molar ratios of TOC/TN and have been corrected for inorganic nitrogen content (0.046%) following the methods of Talbot (2001).

4.5 Results

4.5.1 Core Description

The LINC-1 core (Fig. 4.3) is dominantly marl with as much as 94% TC (Fig. 4.4). The basal unit of the core consists dominantly of clay and gravel capped by a 2 cm grey clay layer at 7.2 m, overlain by a thicker clay layer from 6.6 m to 6.4 m. This is in turn overlain by tan coarse marl to 4.8 m where there is a transition to brown non-laminated marl until 2.1 m. A layer with high peat content from 2.1 m to 2.0 m underlies tan marl with few laminations that persists until 1.25 m. This is succeeded by highly fossiliferous peat. Peat dominates the sediment between 0.5 m and 0.3 m, in turn overlain by an interbedded peat-marl lens and then peat to the top of the core. The gap in the core (Fig. 4.3) is the result of the high compressibility of peat during the coring process as well as a large piece of wood in the core. Differential compressibility of marl, peat, and wood excludes the possibility to realistically remove compression from the 1st meter of sediment and consequently the isotope data from this section has been omitted.

4.5.2 Radiometric Dating of Sediments

Age control was established by AMS ^{14}C dating (University of Arizona) of carbonate macrofossils, bulk calcite, and organic matter from LINC-1 and LINC PC-1 (Table 2.2, Fig. 4.4). Radiocarbon dates on LINC-1 bulk calcite and macrofossil components are affected by the hard water effect (reservoir effect) that was quantified by comparing contemporaneous wood and carbonate macrofossils in LINC PC-1. The difference between wood and macrofossil samples is 1575 ^{14}C years and was used to correct LINC-1 macrofossil dates. Macrofossil dates, as well as the uppermost organic sample, were converted to calendar years before 1950 (cal. yr B.P.) using CALIB 4.3 (Stuiver et al., 1998a, b). Our age model is based on linear interpolation between calibrated ages yielding a basal age of 16,750 cal. yr B.P., contemporaneous with the first accumulation of late-glacial sediments at Tory Hill (O'Connell et al., 1999). It is possible that the stratigraphically lowest date is offset by a larger hard water effect as $\delta^{13}C_{calcite}$ values at this depth are ~2.5‰, similar to the bedrock $\delta^{13}C_{calcite}$

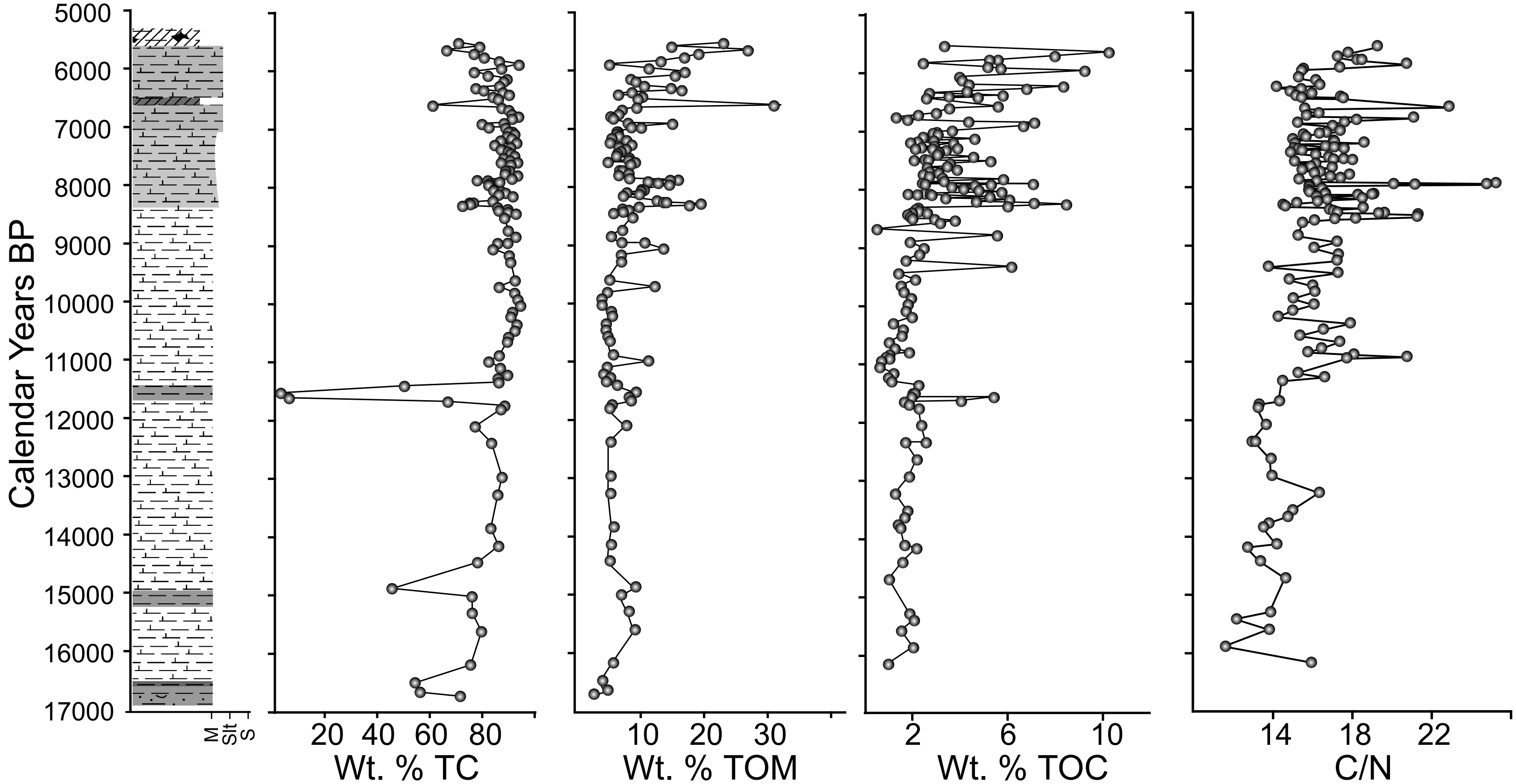

Figure 4.4. Total calcite, total organic matter, total organic carbon, and total nitrogen as weight percents verses calendar years BP.

of 3.2‰. This suggests that calcite at this depth is derived primarily from Paleozoic bedrock carbon devoid of ^{14}C. Therefore, our age model estimate of the basal sediments could be up to 1900 years too old based on wiggle matching $\delta^{18}O_{calcite}$ values from LINC-1 (data not shown) with the GISP2 $\delta^{18}O_{ice}$ record. This would result in younger ages below 6.7 m and a new basal age of 14,480 cal. yr B.P.

4.5.3 Chemostratigraphic Unit Division

The LINC-1 has been divided into five units based on changes in chemostratigraphy for interpretation. These units were defined based on first order trends in carbon isotope stratigraphy as well as lithological changes in the sediment record. We define Unit 1 from the base of the core to 11,600 cal. yr B.P. consisting of dark grey sediment and the general decrease in $\delta^{13}C_{org}$ values. We define Unit 2 as clay rich sediment with higher $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values between 11,600 and 11,300 cal. yr B.P. Unit 3 displays a decrease in $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values between 11,300 and 9,900 cal. yr B.P. Relatively invariant $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values from 9,900 and 8,800 cal. yr B.P. characterize Unit 4. Unit 5 displays a slight increase in $\delta^{13}C_{org}$ values and increased variability in $\delta^{13}C_{calcite}$ values and C/N ratios above 8,800 cal. yr B.P.

4.5.4 Elemental and Isotopic Composition of Bulk Sediment

TOM (Fig. 4.4) is characterized by small changes (2% to 18%) throughout the core while TC fluctuates between 75% and 95%. However, several large anomalies deviate from this general trend at 16.5 ka, 14.8 ka, and 11.7 ka. TOC is low with values ~2% from the base of the core to ~11.4 ka where there is an increase to ~5%. TN generally covaries with TOC with values ranging between 0.2% and 0.8% (data not shown). C/N ratios (Fig. 4.5) demonstrate a small increasing trend from 11 to 26. $\delta^{13}C_{org}$ values (Fig. 4.5) generally covary with $\delta^{13}C_{calcite}$ values through Units 1, 2, and 3 with general decreasing trends. $\delta^{13}C_{org}$ values range from –22.7 to –34.5‰ while $\delta^{13}C_{calcite}$ values range from 2.7 to –9.2‰.

4.5.5 Vegetation and Bedrock Samples

Bedrock in this region is dominated by Visean Carboniferous limestone. The $\delta^{13}C_{calcite}$ value of the bedrock was determined in several locations near the lake and at a site 7 km to the northeast near Gortlecka (Fig. 4.1). $\delta^{13}C_{calcite}$ values average 3.4‰VPDB. We also determined the $\delta^{13}C_{org}$ value for several modern terrestrial plants in the region to characterize the $\delta^{13}C$ value of terrestrial detrital inputs and are shown in Table 4.1. $\delta^{13}C$ values of terrestrial plants in the area are between –27.1‰ and –31.7‰, falling within the range of typical C_3 plants (Vogel, 1993). C/N values fall between 22 and 199. We also analyzed several Charaphytes at Lough Inchiquin that display $\delta^{13}C$ values that range from –35.9‰ to –43.5‰. Surprisingly, the TN values of the modern Charaphytes are rather variable thereby creating large C/N variations. Charaphyte stems have C/N values of 40, which is much higher than the standard C/N ratio of 20 (Meyers, 1994) used to characterize plants as terrestrial in origin.

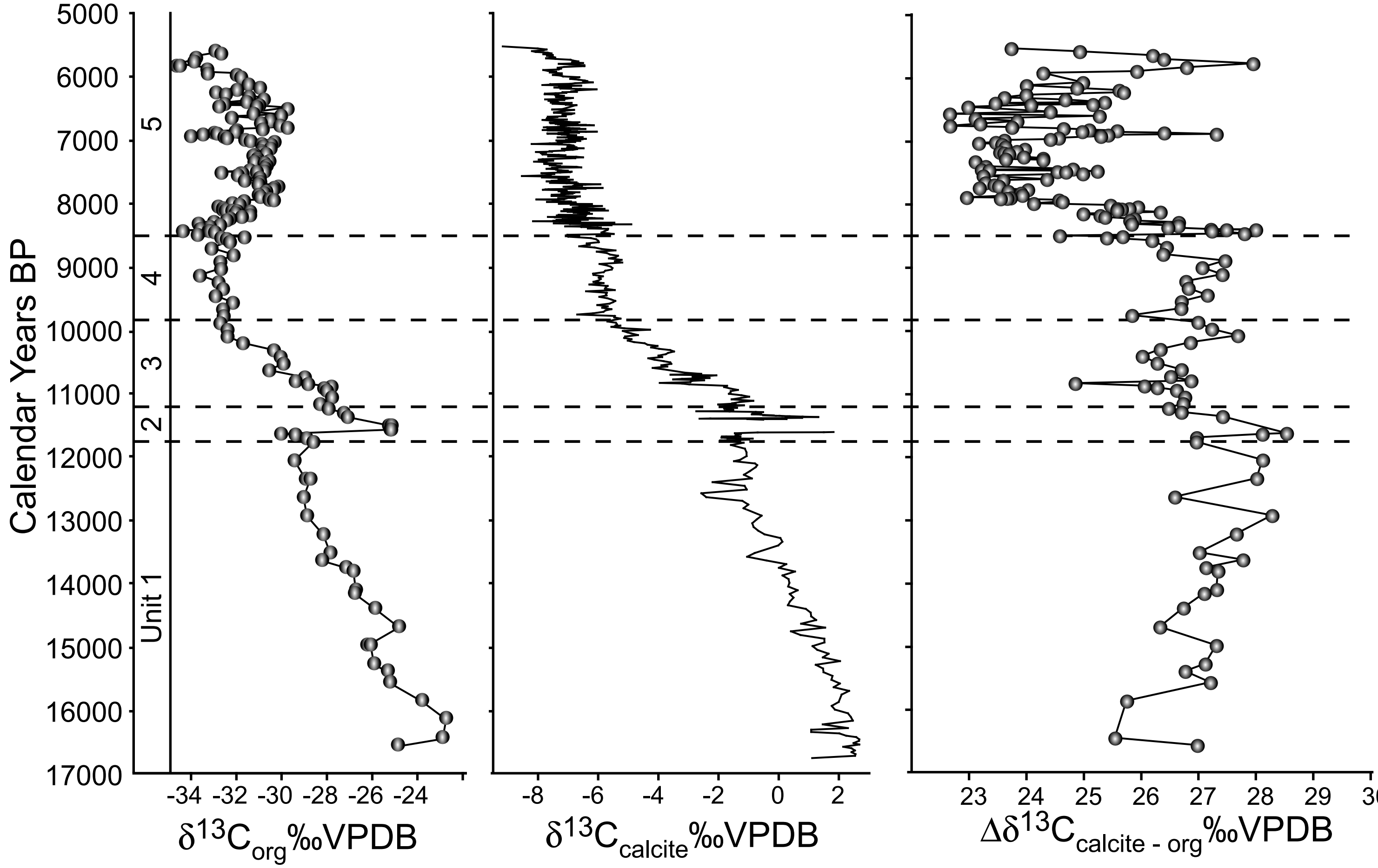

Figure 4.5. $\delta^{13}C_{org}$, $\delta^{13}C_{calcite}$, and $\Delta\delta^{13}C_{calcite - org}$ verses calendar years BP.

Table 4.1. Various Isotope Data

Organic material analyzed	$\delta^{13}C$‰ VPDB	$\delta^{15}N$‰ AIR	TOC (%)	TN (%)	C/N ratio
Poaceae	-27.1	3.1	45.6	2.1	25.1
Poaceae	-25.3	4.3	45.9	0.7	76.3
Poaceae *Danthonia*	-27.3	-1.1	46.4	0.3	199.2
E. *Calluna vulgaris*	-30.4	-4.5	47.5	1.3	44.2
A. *Acer pseudoplatanus*	-29.3	2.8	38.2	2.0	22.2
P. *Athyrium filix-femina*	-26.4	-0.9	43.1	0.6	85.8
B. *Alder glutinosa*	-29.5	-0.4	38.6	1.9	24.2
C. *Carex*	-30.6	3.0	43.5	1.7	30.6
C. *Carex*	-30.2	1.1	43.1	1.4	35.4
Unidentified shrub	-31.7	1.3	46.9	2.0	26.9
Chara #1	-39.0	5.5	42.8	3.7	13.5
Chara #2 (stem)	-43.5	6.9	46.0	1.3	39.9
Chara #2 (leaves)	-38.4	6.3	43.5	4.4	11.6
Chara #3	-35.9	5.0	42.8	3.2	15.8
Chara #4	-42.3	6.1	45.1	2.4	22.2
Chara #5 (large leaf)	-41.5	6.4	44.5	2.1	24.2
Chara #5 (small leaf)	-28.7	5.0	41.9	3.3	14.8
Peat (4250 cal. yr B.P.)	-29.1	4.2	47.4	3.0	18.5
Peat (4275 cal. yr B.P.)	-29.2	3.8	46.4	3.1	17.6

Calcite Material Analyzed	
Chara #1	-9.10
Chara #2	-8.68
Chara #3	-8.81
Chara #4	-8.78
Burren Limestone (near Inchiquin)	3.38
Burren Limestone (near Inchiquin)	3.32
Burren Limestone (near Gortlecka)	3.19
Burren Limestone (near Gortlecka)	3.37
Burren Limestone (near Gortlecka)	3.63

4.6 Discussion

4.6.1 Lacustrine Carbon Dynamics

Variations in carbon isotope values of calcite and organic sediments in lakes is complicated and often unconstrained. At Lough Inchiquin, variations in $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ are too large to discuss without introducing a model of lacustrine carbon cycling dynamics in lakes (Fig. 4.6; Table 4.2). Our model of carbon isotope variability at Lough Inchiquin will clarify the interpretation of sediment values.

Weathered carbon is primarily transferred into the lake system in this highly karstified region via two primary pathways: surface water ($\delta^{13}C_{W\text{-}SW}$; river or sheet run off) and through groundwater ($\delta^{13}C_{W\text{-}GW}$). $\delta^{13}C$ values of the these two pathways are controlled by proportionality of the weathering flux of limestone (bedrock $\delta^{13}C_{calcite}$ constant), the weathering flux of terrestrial organic material ($F_{W\text{-}org}$) and the respective carbon isotope values ($\delta^{13}C_{W\text{-}org}$). Weathering of the limestone bedrock ($\delta^{13}C_{calcite}$ = 3.4‰) will supply HCO_3^- with $\delta^{13}C$ values between 3.5‰ and 2.5‰ (5˚C to 25˚C respectively; Mook, 1986). The $F_{W\text{-}org}$ includes incorporation of CO_2 derived from the oxidation of soil organic matter derived from terrestrial vegetation. Carbon is also transferred into the lake via surface water or groundwater from the breakdown of terrestrial organic material as Particulate Organic Carbon (TPOC; POC will refer to aquatically derived sources). The flux of TPOC into the lake system (F_{TPOC}) will change through time with the development of vegetation and through variations in the $\delta^{13}C_{TPOC}$. Carbon is also transferred into the lake through exchange of atmospheric CO_2 with the lake system. The flux of atmospheric CO_2 (F_{atm}) in and out of the lake is likely balanced through time resulting in no net isotope shifts. $\delta^{13}C$ values of HCO_3^- in equilibrium with CO_2 gas with an atmospheric value of –6.7‰ (Keeling et al., 1979) will range from 3.7‰ and 1.4‰ (5˚ to 25˚C respectively; Mook et al., 1974).

Within the lake system, the $\delta^{13}C_{DIC}$ values will be determined by relative contributions of exogenous carbon and the internal carbon cycle. The internal carbon cycle is controlled by the burial of aquatic organic carbon ($F_{org\text{-}aq}$), burial of carbonate carbon ($C_{calcite}$), and respired carbon released (F_{res}) from buried carbon. The internal carbon cycle results in subseasonal variations in $\delta^{13}C_{DIC}$ values (e.g., Hollander and McKenzie, 1992). The isotope value of carbonate ($\delta^{13}C_{calcite}$) is influenced by $\delta^{13}C_{DIC}$ values and calcite-HCO_3^- fractionation ($\Delta_{calcite\text{-}HCO3-}$) determined by Mook (1986).

Carbon isotope values of aquatically derived organic carbon ($\delta^{13}C_{org\text{-}aq}$) is determined by $\delta^{13}C_{DIC}$ values that are in turn influenced by the uptake and assimilation of carbon by plants (ε_p). ε_p is difficult to determine because the predominate carbon fixers at Lough Inchiquin are Charaphytes that are common throughout the sediment record based on the plethora of fine-grained marl and macrofossil remains. Charaphytes utilize carbon from HCO_3^- for photosynthesis and precipitate

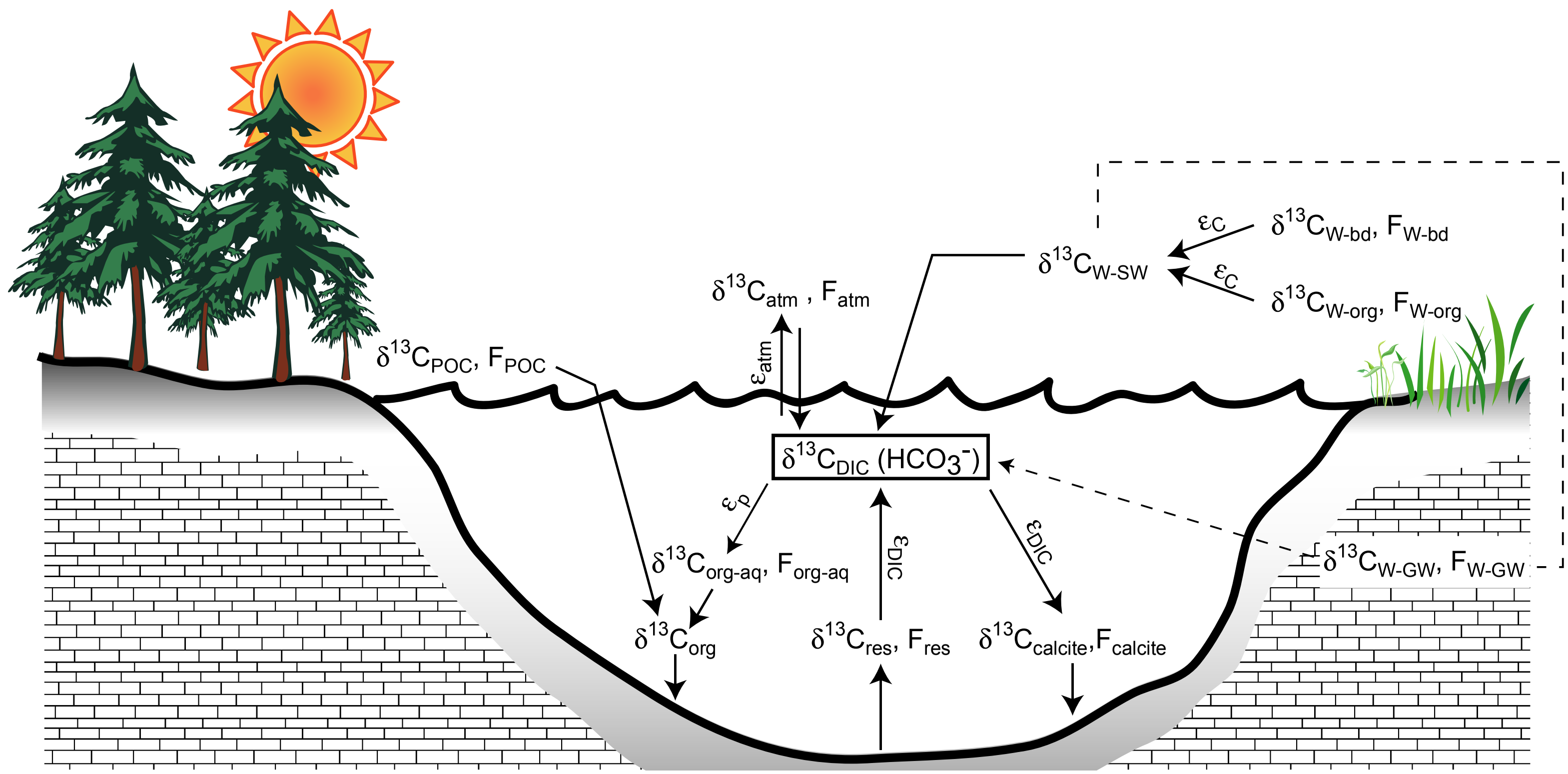

Figure 4.6. Carbon cycle illustration for freshwater lake systems. See Table 4.3 for variables.

Table 4.2. List of Variables

Variable	Definition
aq	Aquatic derived carbon from primary producers
atm	Atmospheric carbon source
bd	Bedrock derived carbon
DIC	Dissolved inorganic carbon
F	Flux rate
GW	Ground water source
org	Organic carbon
res	Respired carbon
SW	Surface water source
TPOC	Terrestrial particulate organic carbon
W	Weathered Carbon
ε_{atm}	Carbon isotope fractionation (HCO_3^- - CO_2 g)
ε_C	Carbon isotope fractionation (calcite - HCO_3^-)
ε_{DIC}	Carbon isotope fractionation (HCO_3^- - CO_2 aq)
ε_p	Carbon isotope fractionation from photosynthesis

calcite through proton pumping (Hammarlund et al., 1997; McConnaughey, 1991; McConnaughey and Falk, 1991). The net ε_p associated with Charaphytes has not been empirically determined. Determination of ε_p in aquatic plants is also complicated because it is difficult to constrain whether carbon is assimilated by passive diffusion of CO_2 and/or active transport of HCO_3^-. Typical values for ε_p range from 21 to 28‰ (Pace et al., 2004). Carbon isotope values of organic carbon that is buried ($\delta^{13}C_{org}$) is determined by the flux and isotope values of two different components: aquatic organic carbon from primary production and the influx of TPOC. It is important to note that the F_W is different than the F_{TPOC} because the F_W will affect the DIC directly whereas the F_{TPOC} will not unless it is oxidized after entering the lake system.

4.6.2 Secular Variations in Carbon Inputs

$\delta^{13}C_{org}$ values at the base of Unit 1 are the highest values in the sediment record. Values this high are not uncommon in lakes where the primary carbonate species is bicarbonate (Hammarlund et al., 1997, Laws et al., 1995) and the dominant aquatic vegetation are Charaphytes. The magnitude of change in $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values and the analogous trends in $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values from 16.8 ka to 8.5 ka (Fig. 4.5) must be in response to variations in the $\delta^{13}C_{DIC}$ values. We propose that at end of the Pleistocene terrestrial vegetation increased in the form of pioneer vegetation communities. This resulted in progressive soil development which allowed for the development of soil CO_2 from the decay of C_3 vegetation with $\delta^{13}C$ values between –24% and –30‰ (Vogel, 1993), similar CO_2 values (Leng and Marshall, 2004), supplying HCO_3^- with $\delta^{13}C_{w\text{-}org}$ between –14‰ and –20‰, depending on the temperature (Mook et al., 1974; Leng and Marshall, 2004). Increased vegetation results in higher $F_{W\text{-}org}$ compared to $F_{W\text{-}bd}$, which forces a decrease in $\delta^{13}C_{DIC}$ values resulting in the observed decrease in $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values. Changes in the terrestrial vegetation force changes in DIC that have been identified in Sweden wherein a change from a pioneer herb community to boreal forests in the early Holocene resulted in decreasing $\delta^{13}C_{DIC}$ values of the in groundwater (Hammarlund et al., 1997). The influence of bedrock carbon and soil CO_2 on DIC in lacustrine systems have been identified elsewhere as well (Aravena et al., 1992; Andrews et al., 1997; Leng et al., 1999).

The decrease in $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values from 16.8 to 8.5 ka is intrinsically related to decreasing $\delta^{13}C_{DIC}$ values as a result of increased soil formation. The large magnitude of change at Lough Inchiquin is to be expected because of the lack of terrestrial vegetation and soils following deglaciation in western Ireland (~17,400 cal. yr B.P.; Bowen et al., 2002) inferred from nearby pollen records and clay rich sediments at the base of Unit 1 (Fig. 4.3). The trend from high to low $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values in Unit 1 can not be caused by changes in the F_{TPOC} because this would require oxidation of the TPOC to be utilized by Charaphytes for calcite precipitation. $\delta^{13}C_{org}$ can be affected by the F_{TPOC} and is identified by increasing C/N ratios because terrestrial plants have values generally above 20 (Meyers et al., 1994). C/N ratios at Lough Inchiquin increase only slightly from 16.8 to 8.5 ka and therefore the F_{TPOC} was relatively constant if C/N ratios are a reliable measure of terrestrial inputs.

During climate perturbations that are cold and/or dry, vegetation and soil development decrease resulting in decreasing $F_{W\text{-}org}$ and thereby forcing higher $\delta^{13}C_{DIC}$ values. This appears to be the case at ~14.9 ka concurrent with the Oldest Dryas Stadial event (Stuiver et al., 1995) identified in $\delta^{18}O_{calcite}$ data from Lough Inchiquin (see Chapter 3). During this interval, an increase in $\delta^{13}C_{org}$ values of almost 2‰, indicates decreased $F_{W\text{-}org}$ and increased $F_{W\text{-}bd}$ from weathering of bedrock. This may be explained by rapid erosion of bedrock and soils during this time (O'Connell et al., 1999; Watts, 1984) resulting in decreased contributions of soil CO_2 in the F_W. More pronounced is the transition at the base of Unit 2 corresponding to the latter part of the YD. At 11.8 ka, a small decrease in $\delta^{13}C_{org}$ values (1.4‰) may reflect increased erosion resulting in increased F_{TPOC} concurrent with increasing C/N ratios and increasing TOC. During the YD in this region, the primary plant communities are herbaceous (Watts, 1984) with low soil stability and likely assisting in rapid soil erosion. The collapse in vegetation at 11.6 ka is extreme based on the ~5‰ increase in $\delta^{13}C_{org}$ and ~4‰ in $\delta^{13}C_{calcite}$ suggesting low contributions of $F_{W\text{-}org}$. Interestingly, the increase $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values does not occur with the onset of the YD around 13,800 cal. yr B.P. (Stuiver et al., 1995; O'Connell et al., 1999) but instead at 11.8 ka. This suggests that the vegetational landscape may have only slightly been modified during the majority of the YD and climate during the YD in Ireland shifted substantially at 11.8 ka such that $F_{W\text{-}org}$ decreased.

Following the rapid increase in $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values in Unit 2, a rapid decrease in values continues to the top of Unit 4. This transition from high to low values occurs within ~1500 years, in contrast to the much longer transition in Unit 1 of ~4,500 years. We attribute this rapid recovery in Units 2 and 3 to the rapid reestablishment of vegetation following the YD subsequently resulting in increased $F_{W\text{-}org}$. Though colder conditions during the YD would have limited vegetation expansion, pollen records indicate that vegetation did persist through the YD. Vegetation would have therefore recovered more rapidly following the YD than in earlier periods. $\delta^{13}C_{org}$ values do not return to values as high as at the base of Unit 1, indicating that the soil was not completely lost during the YD. The rapid establishment of pioneer vegetation and ultimately establishment of wooded areas with birch likely resulted in rapid soil development. This resulted in increased $F_{W\text{-}org}$ and subsequent decreased $\delta^{13}C_{DIC}$ values.

$\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values remain nearly constant in Unit 4 suggesting this is a steady state period with respect to $F_{W\text{-}org}$ and $F_{W\text{-}bd}$. This period is followed by a transition to Unit 5 with an increasing asymmetric trend in $\delta^{13}C_{org}$ values that is penecontemporaneous with increasing variability in C/N ratios. The variability of $\delta^{13}C_{org}$ values and C/N suggests differences in the relative contributions of F_{TPOC}. Modern terrestrial organic matter from this area has $\delta^{13}C_{org}$ values between –25.3 and –31.7‰ and C/N ratios above 22.2. Charaphytes also have high C/N ratios but low $\delta^{13}C$ values, which would not explain the observed increase. The increase may reflect small contributions of peat growing around the lake margin increasing the F_{TPOC}. Peat isolated from 4.2 ka (no modern samples collect) has $\delta^{13}C_{org}$ of –29.1 and C/N values of ~19 and may have had similar values during Unit 4. Regardless of the source of carbon, the carbon must not be oxidized because the $\delta^{13}C_{calcite}$ is not altered suggesting that the variation in $\delta^{13}C_{org}$ is predominantly a result of increased F_{TPOC}.

4.6.3 Carbon Isotope Variation

Secular variations in lake system carbon isotope values can be investigated further through evaluation of carbon isotope discrimination between bulk organic and calcite constituents. Changes in the differences between $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ can be elucidated using the equation:

$$\Delta\delta^{13}C_{calcite\text{ - }org} = \delta^{13}C_{calcite} - \delta^{13}C_{org} \text{ (Eq. 4.1)}$$

Equation 4.1 has been used previously by numerous researchers (e.g. Hollander and McKenzie, 1991; Hollander et al., 1992) to evaluate carbon isotope fractionation associated with changes in photosynthetic fixation (O'Leary, 1981) as well as a proxy for pCO_2 (e.g., Arthur et al., 1985; Freeman and Hayes, 1992; Kump and Arthur, 1999; Kump et al., 1999). Decreases in $\Delta\delta^{13}C_{calcite-org}$ have been shown to correlate with decreasing $CO_{2(aq)}$ (O'Leary, 1981; Farquhar et al., 1989; Hollander and McKenzie, 1991; Hollander et al., 1992) and reflects the concentration of dissolved CO_2 in surface waters where calcite is formed in surface waters and organic matter is autochthonous (Popp et al., 1989; Hayes et al., 1989; Hollander and McKenzie, 1991; Hollander et al., 1992). However, the use of $\Delta\delta^{13}C_{calcite-org}$ as a proxy for paleoclimate has many complications such as variations in the ε_p as a result of growth rates and temperatures (e.g. Kump and Arthur, 1999), although no laboratory experiments have been conducted with Charaphytes to determine if variations in ε_p exist. Long-term trends in $\Delta\delta^{13}C_{calcite\text{ - }org}$ should not be expected if there are no changes in ε_p, F_{TPOC}, or oxidation of $\delta^{13}C_{org}$ and values should either reflect equilibrium or a steady state value. Variations in F_{TPOC} can cause $\Delta\delta^{13}C_{calcite\text{ - }org}$ to increase through time if $\delta^{13}C_{TPOC} < \delta^{13}C_{org\text{-}aq}$ or to decrease if $\delta^{13}C_{TPOC} > \delta^{13}C_{org\text{-}aq}$. In lakes that do not have inputs of carbon from weathered marine limestone, the previous relationship would not need to be taken into account because $\delta^{13}C_{TPOC}$ is almost always higher than $\delta^{13}C_{org\text{-}aq}$. However, Lough Inchiquin has $\delta^{13}C_{org\text{-}aq}$ values that are high for the Late Glacial and early Holocene due to contributions of $F_{W\text{-}bd}$.

The majority of the $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ variation at Lough Inchiquin has been shown to represent variations in $\delta^{13}C_{DIC}$ values and that $\Delta\delta^{13}C_{calcite-org}$ can be used to examine smaller variations in carbon isotopes to constrain variations in the F_{TPOC} and possibly $\delta^{13}C_{TPOC}$ values. A study of POC in small lakes in the USA has determined that ~50% of the POC was derived from TPOC (Pace et al., 2004) indicating that the F_{TPOC} is a significant source of carbon in lake systems.

In this study, differing sampling resolution (ranges from 0.2 cm and 0.05 cm) in the $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values results in $\Delta\delta^{13}C_{calcite-org}$ (Fig. 4.6) that does not represent the same time integration. However, large-scale processes such as soil development occur over much longer timescales than calcite precipitation, therefore the $\Delta\delta^{13}C_{calcite-org}$ equation is still useful for interpreting changes in the carbon cycle of the lake system.

$\Delta\delta^{13}C_{calcite-org}$ increases from 16.5 to 13 ka. This increase is caused by increasing F_{TPOC}. As F_{TPOC} increases, $\delta^{13}C_{org}$ values decrease to reflect greater contributions of TPOC with low $\delta^{13}C_{TPOC}$ values (modern terrestrial organic material –27.1 to –31.2‰, Table 4.1) in comparison to higher $\delta^{13}C_{org\text{-}aq}$ at this time. TPOC could be in the form of cellulose or lignin and has been shown by Sauer et al. (2001) to be resistant to degradation and did not result in changes in C/N ratios. Development of terrestrial vegetation at this time is significant because of the decrease in $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values and because there must be increasing amounts of terrestrial detritus. The increase in $\Delta\delta^{13}C_{calcite-org}$ could be related to increasing ε_p imparted by Charaphytes, which have been suggested to impart significant kinetic effects as a result of proton pumping (Hammarlund et al., 1997; McConnaughey, 1991; McConnaughey and Falk, 1991). During photosynthesis, discrimination against ^{13}C within Charaphytes results in relatively higher $\delta^{13}C$ values of CO_2 supplied to the site of calcite precipitation (Hammarlund et al., 1997) resulting in increased differences between $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$.

Following the end of the YD, $\Delta\delta^{13}C_{calcite-org}$ values decrease by several ‰. This may be explained by a reorganization of the carbon fluxes in the lake to reflect decreased F_{TPOC}. Values from 11.2 to 9 ka increase similarly to values in Unit 1, however the magnitude of variation is smaller. The magnitude of the variation may be small at this time because there is a transition of $\delta^{13}C_{org\text{-}aq} > \delta^{13}C_{TPOC}$ to $\delta^{13}C_{org\text{-}aq} < \delta^{13}C_{TPOC}$.

The rapid decrease at 9.0 ka (Fig. 4.6) is the result of a change in the F_{TPOC} into the lake system. This correlates with increased variability in the C/N ratios, however $\delta^{13}C_{calcite}$ values are relatively constant in Unit 5. This can only be explained by an increase in F_{TPOC}. The TPOC increase could be caused by an increase in the $\delta^{13}C_{TPOC}$ as well from the input of resistant organic material such as lignin and/or cellulose (Sauer et al., 2001) with higher $\delta^{13}C$ values. Terrestrial cellulose in arctic lake studies was determined to be several thousand years older than the bulk organic sediment suggesting that the cellulose is very resistant to weathering and that there is a considerable time-lag in the transport to the sediment (Sauer et al., 2001). Pollen records support significant increases in pine, oak, hazel, and elm at ~10 ka nearby to Lough Inchiquin at Gortlecka (Watts, 1985). It would seem reasonable that cellulose, lignin, and other TPOC components would have been common by 1000 years after initiation of woodland development. This development should result in a decrease in $\Delta\delta^{13}C_{calcite-org}$. Higher $\delta^{13}C_{org}$ values, a slight decrease in TC, and an increase in TOC at this time may also correlate with a switch from oligotrophic to eutrophic conditions in the lake (e.g. Dean, 1999).

4.7 Conclusion

Our study of Lough Inchiquin utilizes carbon isotope values of calcite and bulk organic material, along with TC, TOM, TOC, TN, C/N ratios, and lithological characteristics to evaluate changes in climate and terrestrial vegetation. The relative proportions of carbon from soil versus limestone bedrock in the flux of weathered carbon input to lake system varied through time as a result of variations in terrestrial vegetation. This results in variations in $\delta^{13}C_{DIC}$ values and subsequent variations in $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ values. During periods of increasing terrestrial vegetation and subsequent soil development, $\delta^{13}C_{org}$ and $\delta^{13}C_{calcite}$ decrease significantly. During the Late Glacial period and early Holocene, development of terrestrial vegetation and subsequent soils resulted in an increased flux of weathered carbon derived from soils resulting in decreasing $\delta^{13}C_{DIC}$ values. Environmental perturbations, such as the Oldest Dryas and Younger Dryas stadial events are manifested in the record as a return to higher $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values forced by a decreased flux of terrestrial carbon, and increased erosion of limestone bedrock in response to decreased vegetation. Proper interpretations of carbon isotope records in lake sediments therefore require an understanding of the flux of carbon from soils and limestone bedrock.

4.8 Acknowledgements

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4.10 Manuscript's Relationship to the Thesis

Chapter 4 presents a record of $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ variability and terrestrial vegetation development through the Late Glacial and early Holocene at Lough Inchiquin in western Ireland. This chapter is directly related to the thesis as this chapter provides evidence for climate variability. This is different than Chapter 3 because it provides evidence for landscape changes rather than changes driven by atmospheric circulation and/or temperature. However, both chapters provide information that is relevant for defining climate variability in western Ireland.

CHAPTER 5. DISCUSSION AND RELATION OF THE MANUSCRIPTS TO THE THESIS

Each manuscript (Chapter 2, 3, and 4) included in this thesis is intrinsically related to each other by the application of stable isotopes to determine different aspects of Irish climate during the Late Glacial, Early Holocene, and the modern.

Chapter 2, Survey of Stable Isotope Values in Irish Surface Waters, provides the first regional survey of surface water isotope values for Ireland, which is useful for characterizing modern meteorology and providing a template for comparison of lake sediment-based paleoclimate records. This study is different from other hydrological studies because it evaluates surface water stable isotope values instead of precipitation stable isotope values. This is advantageous in paleolimnological studies because surface water isotope values will be most closely related to the values ultimately recorded by the stable isotope values of lacustrine sediment. The snapshot of modern isotope variability is ideal for evaluating surface water isotope variation by providing insights into spatial variations in contemporary atmospheric circulation and climate conditions. The short field season during summer is particularly appropriate because lake sediment calcite is generally only precipitated during the summer months by charaphytes and therefore the summer surface water values are more important than an average surface water value. This is especially true in western Ireland where the residence times of lakes (particularly turloughs) may be less than 1 month (Allott, N.A., personal comm., 2004).

The study undertaken in Chapter 2 is ideal if multiple lake records from different locations in Ireland are to be compared. In the future, this could provide a basis for development of paleocirculation maps for Ireland from the comparison of well-dated lacustrine sediment records.

Chapter 3, Evidence for High Frequency Late Glacial to mid-Holocene (16,800 to 5,500 calendar years BP) Climate Variability from Oxygen Isotope Values of Lough Inchiquin, Ireland, provides a continuous archive of western Ireland paleoclimate between 16,800 and 5,500 cal yr B.P. from $\delta^{18}O_{calcite}$ values and other geochemical information from a sediment core taken from Lough Inchiquin, County Clare, Ireland. Ireland is particularly sensitive to climate variability because it is located in the eastern Atlantic Ocean where minor changes in thermohaline circulation, oceanic circulation, atmospheric circulation, and the NAO have a significant effect on the $\delta^{18}O_{precipitation}$ and therefore the $\delta^{18}O_{calcite}$ values. The climate of Ireland was highly variable through the Late Glacial and early to mid Holocene evidenced by high-frequency variability in $\delta^{18}O_{calcite}$. Several previously undescribed climate anomalies in western Ireland were identified in this study at 10,800 and 7,100 cal. yr B.P. Additionally, increased winter precipitation between 7,300 and 6,700 cal. yr B.P. is likely responsible for the significant decrease in $\delta^{18}O_{calcite}$ values. This is the first high-resolution climate record for western Ireland that extends back to 16,800 cal. yr B.P. providing evidence for rapid climate variability in western Ireland during the Late Glacial and the early Holocene.

Chapter 4, Landscape and Climate Change from 16,500 to 5,300 Calendar Years Before Present at Lough Inchiquin, Western Ireland Inferred from a Multiproxy Study of Lake Sediment, incorporates carbon isotope values of calcite and bulk organic material, as well as other geochemical data and lithological characteristics to interpret lake sediment data in response to terrestrial vegetation changes. During the Late Glacial period and early Holocene, establishment of terrestrial vegetation and subsequent soils resulted in an increased flux of weathered carbon derived from soils resulting in decreasing $\delta^{13}C_{DIC}$ values. Environmental perturbations, such as the Oldest Dryas and Younger Dryas stadial events appear in the record as a return to higher $\delta^{13}C_{calcite}$ and $\delta^{13}C_{org}$ values indicative of an increased flux of weathered bedrock carbon, indicating increased erosion in response to decreased vegetation.

APPENDIX A. IRISH SURFACE WATER DATA

Irish surface water sample data with location and date sampled. (N.A., not available; RD, rivers downstream of lakes; RU, rivers unrelated to lakes; RV, reservoir; OM, ocean mixing; L, lakes)

Sample Site	Smp. #	Date	Latitude dc. dgs.	Longitude dc. dgs.	Grid Location Gr. #	East	North	Elev. (m)	$\delta^{18}O$ (‰, VSMOW)	δD (‰ VSMOW)	d-excess	Type
An Forghas - Ballyhee	1	7/8/03	52.885	-8.986	IR	33671	81993	14	-5.64	-39.8	5.3	RD
Teeronaun	2	7/8/03	52.893	-9.007	IR	32228	82911	13	-5.48	-38.5	5.4	RU
Loch Dhrom Mor	3	7/8/03	52.923	-8.962	IR	35291	86206	14	-5.65	-36.8	8.3	L
Loch Mhuicennach	4	7/8/03	52.977	-8.936	IR	37163	92229	11	-4.28	-33.9	0.3	L
Loch Bhéal Íochtair	5	7/8/03	52.963	-8.987	IR	33699	90658	13	-4.79	-34.8	3.5	L
Ballard Brooke	6	7/8/03	52.976	-9.006	IR	32444	92125	14	-5.18	-36.0	5.4	RU
Loch Buinne	7	7/8/03	53.014	-8.932	IR	37464	96298	16	-4.27	-33.8	0.3	L
Gort River Downtown	8	7/8/03	53.065	-8.817	IM	45265	01944	40	-5.72	-39.2	6.6	RU
Ballychalan River	9	7/8/03	53.104	-8.752	IR	49657	05648	40	-5.71	-40.8	4.8	RU
Lough Bailyturin	10	7/8/03	53.053	-8.751	IM	49671	00462	38	-5.64	-39.1	6.0	L
Loch Cútra	11	7/8/03	53.036	-8.767	IR	48556	98665	33	-5.59	-40.1	4.6	L
Abhainn Da Loilíoch	12	7/8/03	53.023	-8.769	IR	48417	97190	38	-6.12	-40.4	8.6	RU
Bleach River	13	7/8/03	53.011	-8.640	IR	57033	95711	60	-5.43	-40.2	3.2	RD
Loch Gréine	14	7/8/03	52.966	-8.642	IR	56892	90704	52	-5.84	-40.3	6.5	L
Kilgory Lough	15	7/8/03	52.855	-8.686	IR	53793	78469	34	-5.43	-37.2	6.2	L
Loch Choileáin Uí Shíoda	16	7/8/03	52.826	-8.768	IR	48232	75276	34	-4.66	-34.2	3.1	L
An Forghas an Cora Finne	17	7/8/03	52.838	-8.966	IR	34879	76820	2	-5.57	-38.0	6.5	RD
Poulnacally	18	7/8/03	52.939	-8.950	IR	36125	88055	8	-5.39	-38.4	4.7	RU
An Forghas an Cora Finne	19	7/8/03	52.944	-9.061	IR	28659	88596	10	-5.82	-38.0	8.5	RD
Lough Inchiquin	20	7/9/03	52.951	-9.079	IR	27492	89444	19	-5.85	-37.2	9.7	L
An Forghas	21	7/9/03	52.972	-9.101	IR	26028	91839	27	-5.70	-39.6	6.1	RU
Loch an tSéideain	22	7/9/03	52.951	-9.079	IR	27492	89444	17	-5.75	-38.2	7.7	L
Loch Gallaun - west	23	7/9/03	52.997	-9.024	IR	31279	94505	80	-4.76	-34.7	3.4	L
Loch Gallaun - east	24	7/9/03	52.997	-9.022	IR	N.A.	N.A.	80	-4.93	-37.8	1.7	L
Loch an Leicin	25	7/9/03	52.964	-9.209	IR	18740	91006	71	-4.64	-30.3	6.8	L
An Eidhneach	26	7/9/03	52.938	-9.289	IR	13317	88200	30	-5.25	-35.6	6.4	RU
Derrymore River	27	7/9/03	52.883	-9.199	IR	15953	82007	48	-5.27	-34.2	8.0	RU
Loch Chluam Meacan	28	7/9/03	52.867	-9.193	IR	19700	80230	60	-4.07	-28.9	3.7	L
An Eidhneach	29	7/9/03	52.877	-9.176	IR	20830	81282	54	-5.48	-35.3	8.5	RU
River Shannnon	30	7/10/03	52.662	-8.631	IR	57298	56949	11	-6.41	-43.7	7.6	RD
Abhainn Bhaile na Cloiche	31	7/10/03	52.650	-8.660	IR	55330	55621	8	-6.14	-42.2	6.9	RU
An Mhaigh	32	7/10/03	52.619	-8.766	IR	48134	52303	8	-6.59	-42.8	9.9	RU

River Deel	33	7/10/03	52.604	-8.976	IR	33872	50721	16	-5.94	-38.8	8.8	RU
River At Loghill	34	7/10/03	52.594	-9.194	IR	19070	49915	1	-5.33	-35.1	7.5	RU
River An Gleann	35	7/10/03	52.571	-9.283	IR	13044	47436	5	-5.54	-35.7	8.7	RU
River Feale	36	7/10/03	52.442	-9.477	IQ	99574	33288	10	-5.42	-37.7	5.6	RU
Shanow River	37	7/10/03	52.354	-9.590	IQ	91662	23726	87	-5.78	-37.1	9.2	RU
An Lithe	38	7/10/03	52.256	-9.735	IQ	81554	13013	6	-2.54	-17.0	3.4	OM
An Fhionaghaise	39	7/10/03	52.224	-9.905	IQ	69835	09724	16	-4.64	-30.8	6.3	RU
Abha Mnacha na Bó	40	7/10/03	52.224	-10.130	IQ	54465	10132	35	-4.51	-27.9	8.2	RU
An Scoraid	41	7/10/03	52.215	-10.157	IQ	52593	09182	59	-4.70	-30.2	7.5	RD
River at Rheidiealeara	42	7/10/03	52.187	-10.189	IQ	50278	06110	286	-4.77	-29.5	8.7	RD
Loch an Rheidiealeara	43	7/31/03	52.186	-10.189	IQ	50344	06025	340	-4.65	-29.1	8.1	L
River in Dingle	44	7/11/03	52.141	-10.268	IQ	44786	01177	5	-5.33	-33.3	9.4	RU
Abha Bhaile an Mhuilinn	45	7/11/03	52.141	-10.288	IQ	43357	01279	0	-5.25	-31.0	11.1	RU
Ahaínn an Lóndraigh	46	7/11/03	52.141	-10.164	IQ	51834	00940	35	-5.03	-30.2	10.0	RU
Loch an Scail	47	7/11/03	52.180	-10.073	IQ	58244	05110	77	-4.58	-31.0	5.6	L
Abha an Inligh	48	7/11/03	52.147	-9.963	IQ	65668	01301	8	-5.40	-33.8	9.3	RU
An Mhaing	49	7/11/03	52.166	-9.702	IV	83553	02945	5	-5.58	-36.6	8.0	RU
River Laune	50	7/11/03	52.106	-9.783	IV	77892	96392	8	-6.05	-39.1	9.3	RU
Caragh Lake	51	7/11/03	52.071	-9.869	IV	71879	92663	24	-5.46	-35.1	8.6	L
River Behy	52	7/11/03	52.054	-9.946	IV	66503	90857	14	-4.89	-30.6	8.6	RD
Gleensk River	53	7/11/03	52.031	-10.068	IV	58099	88586	60	-4.80	-29.9	8.5	RU
River Ferta	54	7/11/03	51.966	-10.171	IV	50808	81551	5	-3.50	-27.8	0.1	RU
Abha Chártaínn	55	7/11/03	51.951	-10.204	IV	48465	79944	16	-3.20	-25.8	-0.1	RU
Abhain na Huine	56	7/11/03	51.858	-10.173	IV	50358	69557	4	-4.33	-28.0	6.6	RU
Lough Currane	57	7/11/03	51.823	-10.161	IV	50991	65647	4	-3.86	-27.6	3.3	L
Coomnahcrna River	58	7/11/03	51.771	-10.100	IV	55081	59654	48	-4.07	-29.1	3.4	RU
Sneem River	59	7/11/03	51.838	-9.899	IV	69107	66750	13	-4.34	-24.8	9.9	RU
An Fhinnihe	60	7/11/03	51.880	-9.584	IV	90934	70937	18	-4.35	-28.7	6.1	RU
An tSimhin	61	7/11/03	51.854	-9.587	IV	95240	67948	50	-4.33	-29.3	5.3	RU
An Gleann Garbh	62	7/11/03	51.754	-9.560	IV	92275	56839	182	-3.87	-26.4	4.6	RU
An Mhiolach	63	7/11/03	51.694	-9.440	IW	00471	50027	45	-4.07	-28.1	4.5	RU
River Iiem	64	7/12/03	51.552	-9.263	IW	12401	34033	7	-4.30	-29.0	5.3	RU
Curraghalicky Lake	65	7/12/03	51.668	-9.107	IW	23414	46751	96	-3.97	-28.4	3.4	L
Bandon River	66	7/12/03	51.718	-9.024	IW	29275	52170	73	-4.36	-29.6	5.2	RU
Bhrid River	67	7/12/03	51.843	-8.833	IW	42597	65987	45	-4.94	-33.8	5.7	RU
Beal Na Blath	68	7/12/03	51.821	-8.856	IW	40997	63570	102	-5.12	-33.2	7.8	RU
Taiscumar Resorvoir	69	7/12/03	51.896	-8.788	IW	45730	71851	53	-4.89	-33.3	5.8	RV
Drispey River	70	7/12/03	51.915	-8.745	IW	48799	73899	52	-5.79	-37.9	8.4	RU
Blarney River	71	7/12/03	51.931	-8.567	IW	61022	75650	36	-6.03	-39.0	9.3	RU

River Blackwater	72	7/12/03	52.132	-8.641	IW	56112	97953	45	-5.72	-37.8	8.0	RU
Rine River	73	7/12/03	52.794	-8.921	IR	37866	71867	4	-4.44	-28.5	7.0	RU
Lough Gallaun	74	7/14/03	52.997	-9.024	IR	31279	94505	80	-4.83	-36.6	2.1	L
Loch Coirrib	75	7/14/03	53.496	-9.241	IM	17648	50280	17	-5.28	-34.6	7.6	L
Loch Measca	76	7/14/03	53.597	-9.294	IM	14327	61567	21	-5.09	-36.1	4.6	L
Loch Ceara at Keel Br.	77	7/14/03	53.658	-9.269	IM	16147	68340	39	-4.16	-29.5	3.8	L
Lough Lannagh	78	7/15/03	53.835	-9.339	IM	11827	88126	48	-5.47	-37.2	6.6	L
Clydagh River	79	7/15/03	53.893	-9.259	IM	17258	94460	58	-5.36	-34.5	8.4	RU
Lough Conn	80	7/15/03	53.986	-9.238	IM	18763	04815	16	-5.82	-39.6	7.0	L
Lough Cullin	81	7/15/03	53.978	-9.208	IM	20771	03809	21	-5.16	-34.3	7.0	L
River Moy	82	7/15/03	53.939	-9.102	IM	27625	99362	29	-6.12	-40.2	8.8	RU
River NW of Kiltamgh	83	7/15/03	53.869	-9.010	IM	33574	91582	55	-5.88	-40.5	6.6	RU
Mhaighnwla Manulla River	84	7/15/03	53.817	-9.200	IM	N.A.	N.A.	60	-6.04	-40.0	8.3	RU
An Abhainn Bhui	85	7/15/03	53.801	-9.034	IM	N.A.	N.A.	70	-5.90	-40.7	6.5	RU
Lough Curragh	86	7/15/03	53.779	-8.861	IM	43277	81420	109	-6.06	-41.4	7.1	L
Owengarve River	87	7/15/03	54.001	-8.773	IG	49339	06083	75	-6.26	-40.8	9.3	RU
River near Collooney	88	7/16/03	54.210	-8.502	IG	67257	29110	59	-5.44	-40.0	3.5	RU
River in Sligo	89	7/16/03	54.277	-8.476	IG	69021	36526	8	-5.84	-38.3	8.4	RD
Davis River	90	7/16/03	54.329	-8.501	IG	67443	42332	5	-6.80	-45.4	9.0	RD
Glencar Lake	91	7/16/03	54.339	-8.402	IG	73849	43464	34	-6.52	-44.7	7.5	L
River in Mount Temple	92	7/16/03	54.393	-8.524	IG	65980	49463	28	-6.51	-43.6	8.5	RU
River Erne	93	7/16/03	54.501	-8.189	IG	87784	61399	35	-6.53	-45.1	7.2	RD
Bungosteen River	94	7/16/03	54.654	-8.419	IG	72942	78560	11	-5.12	-36.4	4.5	RU
Owenwee River	95	7/16/03	54.650	-8.644	IG	58434	78169	39	-4.91	-33.7	5.7	RU
Loch O'Mulligan	96	7/16/03	54.627	-8.684	IG	55827	75672	174	-2.39	-21.3	-2.2	L
Abhainn Fhia	97	7/16/03	54.790	-8.286	IG	81621	93596	47	-5.32	-39.2	3.3	RU
Loch Finne	98	7/16/03	54.868	-8.128	IB	91806	02206	160	-5.20	-38.5	3.1	L
Abhainn Ghaoth Beara	99	7/16/03	54.906	-8.206	IB	86763	06466	11	-5.00	-32.5	7.5	RU
Loch Beara	100	7/16/03	54.959	-8.110	IB	92957	12382	95	-5.08	-35.0	5.6	L
Loch Gartáin	101	7/16/03	54.988	-7.913	IC	05554	15634	90	-5.10	-36.4	4.4	L
River Foyle	102	7/17/03	55.002	-7.320	IC	43503	17376	4	-3.66	-24.8	4.5	OM
River Banne	103	7/17/03	55.129	-6.672	IC	84728	32093	7	-5.80	-41.0	5.4	RU
Bush River	104	7/17/03	55.123	-6.469	IC	97681	31749	10	-6.26	-44.6	5.5	RU
Sixmile Water	105	7/17/03	54.715	-6.239	IJ	13468	86633	25	-6.41	-46.2	5.0	RD
Lough Neagh	106	7/17/03	54.716	-6.239	IJ	13486	86748	25	-5.73	-43.3	2.5	L
Lough Island Reavy	107	7/17/03	54.237	-6.021	IJ	29001	33798	122	-5.97	-43.3	4.5	L
River Bam	108	7/17/03	54.177	-6.338	IJ	08511	26633	12	-7.32	-52.7	5.9	RU
Blackwater River	109	7/17/03	53.735	-6.868	IN	74706	76737	54	-6.32	-44.4	6.2	RV
Royal Canal	110	7/17/03	53.525	-7.333	IN	44198	53021	78	-4.43	-30.3	5.2	RV

Lake Ennell	111	7/17/03	53.485	-7.395	IN	40156	48464	82	-5.26	-37.7	4.3	L
River Near Burr	112	7/17/03	53.083	-7.922	IN	05247	03537	40	-6.20	-42.5	7.1	RU
Mulkear River	113	7/17/03	52.669	-8.529	IR	64239	57644	14	-6.02	-38.6	9.6	RU
loch Léin	114	8/1/03	52.043	-9.529	IV	95070	88929	16	-4.63	-35.1	1.9	L
An Fhleise	115	8/1/03	52.047	-9.506	IV	96713	89345	27	-5.03	-32.6	7.6	RU
Loch Mhuerois	116	8/1/03	52.004	-9.530	IV	94973	84703	40	-5.08	-34.8	5.8	L
Galway's River	117	8/1/03	51.964	-9.581	IV	91377	80276	95	-4.99	-33.4	6.5	RU
Loch an Luscánaigh	118	8/1/03	51.956	-9.622	IV	88542	79472	198	-5.08	-32.4	8.2	L
Barfinnihy Lough	119	8/1/03	51.933	-9.670	IV	85148	76912	265	-4.79	-30.6	7.7	L
Owbeg River	120	8/1/03	51.903	-9.471	IV	98757	73343	32	-5.14	-32.2	8.9	RU
An Chlaoideach	121	8/1/03	51.982	-9.313	IW	09832	81894	99	-5.38	-35.6	7.5	RU
Tourig River	122	8/1/03	51.971	-7.864	IX	09378	79877	5	-2.84	-19.6	3.1	OM
Tay River	123	8/2/03	52.172	-7.510	IS	33495	02320	12	-5.81	-39.6	6.8	RU
Mahon River	124	8/2/03	52.201	-7.416	IS	39949	05572	41	-6.08	-38.9	9.7	RU
River Barrow	125	8/2/03	52.395	-6.945	IS	71813	27569	6	-6.16	-42.5	6.7	RU
River Slaney	126	8/2/03	52.501	-6.564	IS	97476	39746	2	-6.60	-42.6	10.2	RU
River Bann	127	8/2/03	52.619	-6.413	IT	07483	53210	28	-6.51	-42.0	10.1	RU
River Woodbridge	128	8/2/03	52.831	-6.234	IT	19020	77061	18	-7.12	-45.2	11.7	RU
River Avoca	129	8/2/03	52.857	-6.213	IT	20396	79955	25	-6.99	-45.8	10.1	RU
Avonmore River	130	8/2/03	53.008	-6.295	IT	14415	96656	144	-6.57	-43.9	8.6	RU
Lough Dah River	131	8/2/03	53.031	-6.251	IT	17346	99229	177	-6.95	-47.0	8.5	RD
Vartry Resevoir	132	8/2/03	53.081	-6.211	ID	19875	04928	239	-6.54	-43.6	8.8	L
Widdow Gap	133	8/2/03	53.023	-6.361	IT	09968	98175	281	-6.10	-42.0	6.8	RD
River Liffey	134	8/3/03	53.131	-6.825	IN	84217	09673	118	-6.85	-45.7	9.1	RD
River Nore	135	8/3/03	52.652	-7.249	IS	50788	55852	61	-6.71	-43.1	10.6	RU
Kings River	136	8/3/03	52.529	-7.395	IS	41043	43997	67	-7.35	-44.9	13.9	RU
Clonmel - NE	137	8/3/03	52.360	-7.641	IS	24483	23168	18	-6.25	-44.4	5.6	RU
River Suir	138	8/3/03	52.352	-7.696	IS	20695	22282	21	-6.38	-43.9	7.1	RU
River Suir	139	8/3/03	52.375	-7.927	IS	04972	24833	51	-6.73	-49.4	4.4	RU
Aherlow River	140	8/3/03	52.418	-7.996	IS	00252	29650	54	-6.44	-41.9	9.6	RU
River in Tipperary	141	8/3/03	52.472	-8.161	IR	89068	35631	92	-5.92	-43.2	4.1	RU
River Dead	142	8/3/03	52.568	-8.258	IR	82481	46341	51	-6.37	-43.0	8.0	RU
Cahernahallia River	143	8/3/03	52.586	-8.254	IR	82775	48277	60	-6.68	-41.9	11.5	RU
an Chlaoideach	144	8/3/03	52.614	-8.333	IR	77478	51492	56	-6.57	-41.6	10.9	RU

APPENDIX B. TOM, TC AND WT. % REFRACTORY VALUES OF LINC-1

Cal. Yr B.P.	Depth (m)	Depth (m, uncorrected)	TOM	TC	Wt. % Refractory
n.a.	0.000	0.400	84.5	9.4	6.1
n.a.	0.050	0.450	83.7	7.2	9.1
n.a.	0.100	0.500	79.2	9.0	11.8
n.a.	0.150	0.550	14.1	70.7	15.2
n.a.	0.200	0.600	5.4	85.8	8.8
n.a.	0.250	0.650	24.3	69.1	6.5
n.a.	0.300	0.700	20.0	75.0	5.0
n.a.	0.350	0.750	32.2	59.6	8.2
n.a.	0.400	0.800	34.8	56.1	9.1
n.a.	0.450	0.850	78.8	14.9	6.3
n.a.	0.500	0.900	88.9	4.2	6.9
n.a.	0.550	0.950	80.4	4.9	14.6
5461	1.000	1.000	23.7	71.1	5.2
5524	1.050	1.050	15.1	79.2	5.8
5586	1.100	1.100	27.8	66.7	5.6
5649	1.150	1.150	19.6	77.0	3.4
5711	1.200	1.200	17.2	80.9	1.9
5776	1.252	1.252	13.3	86.6	0.2
5836	1.300	1.300	4.7	94.1	1.2
5901	1.352	1.352	11.3	87.4	1.3
5961	1.400	1.400	17.3	77.1	5.7
6026	1.452	1.452	15.7	82.3	2.0
6083	1.498	1.498	8.3	89.5	2.2
6126	1.552	1.552	9.1	88.3	2.6
6202	1.652	1.652	10.5	86.7	2.8
6238	1.700	1.700	15.0	77.7	7.3
6277	1.752	1.752	16.8	80.7	2.5
6313	1.800	1.800	8.5	88.0	3.6
6352	1.852	1.852	6.2	90.4	3.4
6389	1.900	1.900	10.2	84.2	5.6
6428	1.952	1.952	9.5	86.3	4.3
6539	2.100	2.100	32.1	61.4	6.5
6578	2.152	2.152	9.2	87.5	3.2
6614	2.200	2.200	6.8	90.2	3.0
6690	2.300	2.300	6.3	91.4	2.4
6729	2.352	2.352	4.9	93.9	1.2
6765	2.400	2.400	5.4	91.5	3.1
6840	2.500	2.500	7.8	88.4	3.8
6857	2.522	2.522	15.2	80.1	4.7
6914	2.598	2.598	8.4	82.7	9.0
6920	2.606	2.606	10.0	89.0	0.9
6991	2.700	2.700	6.1	91.6	2.3
6993	2.702	2.702	6.0	90.1	3.9
7030	2.752	2.752	6.0	92.4	1.6
7066	2.800	2.800	6.3	89.6	4.1
7106	2.852	2.852	5.1	91.3	3.6

7142	2.900	2.900	7.6	87.1	5.3
7181	2.952	2.952	4.8	93.2	2.0
7217	3.000	3.000	8.4	84.9	6.7
7256	3.052	3.052	6.3	90.8	2.8
7292	3.100	3.100	7.5	87.3	5.2
7331	3.152	3.152	6.7	89.9	3.4
7368	3.200	3.200	6.1	90.9	3.1
7407	3.252	3.252	5.9	92.4	1.7
7443	3.300	3.300	8.0	88.3	3.7
7482	3.352	3.352	7.9	90.8	1.3
7517	3.398	3.398	4.5	93.5	2.0
7518	3.400	3.400	9.0	87.3	3.7
7557	3.452	3.452	8.3	90.9	0.8
7660	3.600	3.600	6.4	90.5	3.1
7661	3.602	3.602	6.9	89.0	4.2
7714	3.700	3.700	8.0	88.8	3.3
7743	3.752	3.752	6.3	93.5	0.2
7796	3.848	3.848	8.1	91.4	0.5
7824	3.900	3.900	16.2	78.2	5.6
7825	3.902	3.902	14.8	82.2	2.9
7853	3.952	3.952	11.1	86.7	2.1
7879	4.000	4.000	12.8	82.8	4.3
7907	4.052	4.052	14.7	82.5	2.8
7988	4.200	4.200	10.1	84.7	5.2
7999	4.220	4.220	10.5	84.5	5.1
8017	4.252	4.252	10.0	87.4	2.6
8043	4.300	4.300	7.6	89.0	3.4
8072	4.352	4.352	9.7	86.4	3.9
8099	4.402	4.402	7.0	91.7	1.2
8181	4.552	4.552	12.6	84.2	3.2
8208	4.600	4.600	13.7	75.3	10.9
8210	4.604	4.604	14.2	76.8	9.0
8236	4.652	4.652	19.9	75.6	4.5
8262	4.700	4.700	18.0	72.7	9.3
8291	4.752	4.752	9.6	85.9	4.4
8323	4.810	4.810	6.9	89.8	3.3
8346	4.852	4.852	8.0	86.4	5.7
8372	4.900	4.900	7.0	89.9	3.1
8400	4.952	4.952	5.4	92.9	1.7
8470	5.000	5.000	8.6	88.6	2.8
8690	5.102	5.102	6.9	89.9	3.2
8798	5.152	5.152	5.0	92.8	2.1
8901	5.200	5.200	6.8	89.8	3.4
8905	5.202	5.202	10.6	86.0	3.4
9013	5.252	5.252	13.7	84.2	2.1
9117	5.300	5.300	6.7	90.3	3.0
9233	5.354	5.354	6.7	90.9	2.4
9548	5.500	5.500	4.7	92.6	2.7
9660	5.552	5.552	12.3	86.5	1.2
9763	5.600	5.600	4.4	92.4	3.2

9875	5.652	5.652	3.4	93.6	3.0
9983	5.702	5.702	3.5	94.6	1.9
10091	5.752	5.752	5.0	91.6	3.4
10172	5.790	5.790	5.2	90.9	3.8
10306	5.852	5.852	4.2	93.3	2.6
10414	5.902	5.902	4.1	92.5	3.4
10522	5.952	5.952	4.4	90.0	5.5
10603	5.990	5.990	4.8	89.6	5.6
10840	6.100	6.100	5.4	86.5	8.1
10944	6.148	6.148	11.2	82.6	6.2
11056	6.200	6.200	4.3	87.0	8.7
11173	6.256	6.256	3.7	89.7	6.5
11232	6.300	6.300	4.9	86.1	9.0
11302	6.352	6.352	4.2	86.4	9.4
11366	6.400	6.400	6.0	50.6	43.4
11483	6.488	6.488	9.2	3.8	87.0
11571	6.554	6.554	8.0	7.0	85.0
11633	6.600	6.600	8.3	67.1	24.6
11702	6.652	6.652	5.1	88.6	6.2
11766	6.700	6.700	4.8	87.2	8.0
12063	6.752	6.752	7.6	77.4	15.0
12345	6.800	6.800	4.9	83.6	11.4
12932	6.900	6.900	4.9	87.6	7.4
13237	6.952	6.952	4.9	86.0	9.1
13813	7.050	7.250	5.5	83.3	11.2
14118	7.102	7.302	5.0	86.3	8.7
14400	7.150	7.350	4.8	78.3	16.9
14847	7.226	7.426	9.1	45.9	45.0
14988	7.250	7.450	6.7	76.2	17.1
15270	7.298	7.498	8.0	76.3	15.7
15587	7.352	7.552	9.0	79.8	11.2
16162	7.450	7.650	5.4	75.7	18.9
16468	7.502	7.702	3.6	54.7	41.8
16632	7.530	7.730	4.4	56.6	39.0
16703	7.542	7.742	2.1	71.8	26.1

APPENDIX C. CARBON AND OXYGEN STABLE ISOTOPE VALUES OF LINC-1 BULK CALCITE ANALYSES

Cal. Yr B.P.	Depth (m)	Depth (m, uncorrected)	Saskatchewan Laboratory Number	$\delta^{13}C$ ‰ VPDB	$\delta^{18}O$ ‰ VPDB
n.a.	0.010	0.010	3531	-6.17	-4.99
n.a.	0.012	0.012	6626	-6.36	-5.66
n.a.	0.014	0.014	6627	-6.55	-5.36
n.a.	0.016	0.016	4310	-5.36	-5.29
n.a.	0.018	0.018	6632	-6.63	-5.79
n.a.	0.020	0.020	4311	-5.45	-5.30
n.a.	0.022	0.022	6633	-6.24	-7.23
n.a.	0.024	0.024	6634	-6.32	-6.11
n.a.	0.026	0.026	6636	-6.24	-6.54
n.a.	0.028	0.028	4269	-5.37	-5.28
n.a.	0.030	0.030	3536	-5.38	-5.81
n.a.	0.032	0.032	4270	-5.60	-5.16
n.a.	0.034	0.034	6639	-6.40	-5.38
n.a.	0.036	0.036	4271	-5.35	-5.26
n.a.	0.038	0.038	6641	-6.26	-6.09
n.a.	0.040	0.040	4272	-5.42	-5.24
n.a.	0.042	0.042	6642	-6.23	-6.33
n.a.	0.044	0.044	4273	-5.51	-5.21
n.a.	0.046	0.046	6644	-6.49	-6.65
n.a.	0.048	0.048	4274	-5.54	-5.20
n.a.	0.050	0.050	3541	-5.47	-5.86
n.a.	0.054	0.054	3542	-5.55	-5.95
n.a.	0.056	0.056	4276	-5.33	-5.32
n.a.	0.058	0.058	3543	-5.34	-5.85
n.a.	0.060	0.060	4277	-5.31	-5.23
n.a.	0.062	0.062	3544	-5.42	-5.89
n.a.	0.064	0.064	7339	-6.42	-4.89
n.a.	0.066	0.066	3545	-5.81	-5.77
n.a.	0.068	0.068	6898	-6.60	-5.31
n.a.	0.070	0.070	3546	-5.56	-5.53
n.a.	0.072	0.072	6899	-6.51	-6.06
n.a.	0.074	0.074	6900	-6.59	-5.35
n.a.	0.076	0.076	6901	-6.54	-5.00
n.a.	0.078	0.078	3548	-6.07	-5.12
n.a.	0.080	0.080	3591	-5.55	-5.02
n.a.	0.082	0.082	4258	-5.79	-4.95
n.a.	0.084	0.084	4259	-6.24	-5.33
n.a.	0.086	0.086	4260	-5.76	-4.92
n.a.	0.088	0.088	4261	-6.13	-5.14
n.a.	0.090	0.090	4262	-5.84	-4.95
n.a.	0.092	0.092	4263	-6.01	-5.25
n.a.	0.094	0.094	4264	-5.70	-4.93
n.a.	0.096	0.096	4316	-6.09	-5.51
n.a.	0.098	0.098	4266	-5.11	-5.01

n.a.	0.102	0.102	4280	-5.53	-4.63
n.a.	0.104	0.104	4281	-6.08	-3.97
n.a.	0.106	0.106	4282	-5.49	-4.53
n.a.	0.108	0.108	4283	-5.39	-4.49
n.a.	0.112	0.112	4285	-5.74	-4.90
n.a.	0.114	0.114	4286	-4.42	-5.16
n.a.	0.116	0.116	4287	-7.24	-4.52
n.a.	0.118	0.118	4292	-8.58	-3.68
n.a.	0.120	0.120	4293	-7.74	-3.70
n.a.	0.122	0.122	4294	-6.53	-3.92
n.a.	0.126	0.126	4296	-7.50	-4.52
n.a.	0.128	0.128	4297	-7.15	-4.94
n.a.	0.130	0.130	4298	-5.68	-4.68
n.a.	0.132	0.132	4299	-5.74	-5.04
n.a.	0.134	0.134	4300	-5.62	-5.10
n.a.	0.136	0.136	4301	-5.81	-4.50
n.a.	0.138	0.138	4302	-5.60	-4.81
n.a.	0.140	0.140	4303	-5.56	-5.07
n.a.	0.142	0.142	3560	-5.63	-5.65
n.a.	0.144	0.144	4304	-5.42	-5.37
n.a.	0.146	0.146	4305	-5.62	-5.57
n.a.	0.148	0.148	4306	-5.27	-5.21
n.a.	0.150	0.150	3562	-5.66	-5.11
n.a.	0.152	0.152	4307	-5.24	-5.26
n.a.	0.154	0.154	3563	-5.91	-5.90
n.a.	0.156	0.156	4308	-5.78	-4.63
n.a.	0.158	0.158	3564	-5.52	-5.69
n.a.	0.160	0.160	4309	-6.30	-4.83
n.a.	0.162	0.162	3565	-5.96	-4.80
n.a.	0.164	0.164	4319	-5.76	-5.25
n.a.	0.166	0.166	3566	-5.72	-4.53
n.a.	0.168	0.168	4320	-5.27	-4.59
n.a.	0.170	0.170	3567	-5.47	-4.85
n.a.	0.172	0.172	4321	-5.82	-4.41
n.a.	0.174	0.174	3568	-6.73	-4.94
n.a.	0.176	0.176	4324	-8.10	-3.65
n.a.	0.178	0.178	3569	-7.08	-5.10
n.a.	0.180	0.180	4325	-6.93	-3.83
n.a.	0.182	0.182	3570	-6.88	-4.96
n.a.	0.184	0.184	4326	-6.87	-4.91
n.a.	0.188	0.188	4328	-5.47	-4.49
n.a.	0.188	0.188	4328	-5.35	-4.44
n.a.	0.190	0.190	3572	-5.35	-4.27
n.a.	0.192	0.192	4329	-5.92	-4.80
n.a.	0.194	0.194	3573	-6.32	-5.20
n.a.	0.196	0.196	4330	-5.92	-4.90
n.a.	0.198	0.198	3574	-7.21	-5.12
n.a.	0.200	0.200	4331	-5.49	-5.08
n.a.	0.204	0.204	4332	-5.57	-4.90
n.a.	0.206	0.206	3576	-6.22	-4.61

n.a.	0.208	0.208	4333	-5.86	-4.78
n.a.	0.210	0.210	3577	-5.39	-5.11
n.a.	0.212	0.212	4334	-5.80	-5.20
n.a.	0.214	0.214	4335	-5.87	-5.49
n.a.	0.216	0.216	4336	-5.53	-5.55
5536	1.060	1.060	9511	-9.18	-4.58
5571	1.088	1.088	5681	-8.03	-5.03
5586	1.100	1.100	5680	-7.73	-5.17
5599	1.110	1.110	5679	-7.83	-5.39
5611	1.120	1.120	5678	-8.21	-5.73
5624	1.130	1.130	5677	-8.09	-4.95
5636	1.140	1.140	5676	-7.71	-5.24
5649	1.150	1.150	5675	-7.56	-5.24
5661	1.160	1.160	5674	-7.83	-5.92
5674	1.170	1.170	5673	-7.52	-5.60
5686	1.180	1.180	5672	-7.71	-5.48
5699	1.190	1.190	5671	-7.53	-5.52
5711	1.200	1.200	5670	-7.44	-5.42
5724	1.210	1.210	5682	-7.74	-5.87
5736	1.220	1.220	4828	-7.43	-6.16
5749	1.230	1.230	5683	-6.93	-5.71
5761	1.240	1.240	4827	-6.85	-5.74
5773	1.250	1.250	5684	-6.67	-5.85
5786	1.260	1.260	4826	-6.88	-5.92
5798	1.270	1.270	5685	-6.52	-5.50
5811	1.280	1.280	4825	-7.32	-6.03
5823	1.290	1.290	5686	-6.97	-4.87
5836	1.300	1.300	4824	-6.47	-5.61
5848	1.310	1.310	5687	-6.47	-5.11
5861	1.320	1.320	4823	-7.14	-5.85
5873	1.330	1.330	5688	-7.36	-5.88
5886	1.340	1.340	4822	-7.25	-6.03
5898	1.350	1.350	5689	-7.33	-5.70
5911	1.360	1.360	4734	-7.84	-4.97
5923	1.370	1.370	5693	-7.68	-5.51
5936	1.380	1.380	4733	-7.40	-5.97
5948	1.390	1.390	5694	-7.62	-5.61
5961	1.400	1.400	4732	-7.22	-6.34
5973	1.410	1.410	5697	-7.22	-5.58
5986	1.420	1.420	4731	-7.52	-5.24
5998	1.430	1.430	5698	-7.27	-5.52
6011	1.440	1.440	4730	-7.18	-6.14
6023	1.450	1.450	5699	-6.64	-5.54
6036	1.460	1.460	4729	-6.87	-6.41
6048	1.470	1.470	5700	-6.94	-5.37
6061	1.480	1.480	4681	-6.67	-6.09
6073	1.490	1.490	5701	-6.46	-6.58
6086	1.500	1.500	4680	-6.37	-6.83
6095	1.510	1.510	5702	-6.51	-6.21
6102	1.520	1.520	4679	-6.19	-5.98

6110	1.530	1.530	5703	-6.44	-5.84
6117	1.540	1.540	4678	-6.77	-6.28
6125	1.550	1.550	5704	-6.93	-5.93
6132	1.560	1.560	4677	-7.60	-5.61
6140	1.570	1.570	5705	-7.60	-5.24
6147	1.580	1.580	4728	-7.86	-6.20
6155	1.590	1.590	5706	-6.58	-5.51
6163	1.600	1.600	4727	-7.07	-6.09
6170	1.610	1.610	5707	-7.31	-5.19
6178	1.620	1.620	4834	-6.91	-6.00
6185	1.630	1.630	5708	-7.47	-5.19
6193	1.640	1.640	4696	-7.16	-5.69
6200	1.650	1.650	5709	-7.27	-5.39
6208	1.660	1.660	4695	-6.61	-5.59
6215	1.670	1.670	5710	-6.06	-5.55
6230	1.690	1.690	5711	-6.75	-5.57
6238	1.700	1.700	4693	-6.75	-5.63
6245	1.710	1.710	5712	-6.90	-5.58
6253	1.720	1.720	4692	-6.72	-6.04
6260	1.730	1.730	6598	-7.20	-6.30
6268	1.740	1.740	4691	-7.07	-5.68
6276	1.750	1.750	6599	-7.43	-5.18
6283	1.760	1.760	4690	-7.78	-5.39
6291	1.770	1.770	4842	-7.79	-5.45
6298	1.780	1.780	4689	-7.34	-5.79
6306	1.790	1.790	4853	-7.44	-5.13
6313	1.800	1.800	4688	-7.15	-5.48
6321	1.810	1.810	4852	-7.38	-5.97
6328	1.820	1.820	4687	-7.41	-6.28
6336	1.830	1.830	4851	-7.41	-5.83
6343	1.840	1.840	4686	-7.19	-6.33
6351	1.850	1.850	4850	-6.85	-6.10
6358	1.860	1.860	4685	-7.03	-6.16
6366	1.870	1.870	4849	-7.13	-5.54
6373	1.880	1.880	4684	-7.78	-5.62
6381	1.890	1.890	4848	-7.14	-5.37
6387	1.898	1.898	9510	-7.59	-5.87
6389	1.900	1.900	4683	-7.41	-5.64
6396	1.910	1.910	4847	-7.66	-5.52
6404	1.920	1.920	4682	-7.51	-5.94
6411	1.930	1.930	4846	-7.37	-6.32
6419	1.940	1.940	4836	-7.34	-6.56
6425	1.948	1.948	9509	-7.59	-6.38
6426	1.950	1.950	4845	-6.89	-5.48
6434	1.960	1.960	4672	-7.00	-5.48
6441	1.970	1.970	4844	-7.53	-5.45
6449	1.980	1.980	4671	-7.06	-5.37
6456	1.990	1.990	4843	-7.09	-5.35
6462	1.998	1.998	9508	-6.73	-6.48
6464	2.000	2.000	4670	-6.75	-6.12

6524	2.080	2.080	6597	-7.20	-6.17
6532	2.090	2.090	6596	-7.54	-6.25
6539	2.100	2.100	6595	-6.81	-5.79
6547	2.110	2.110	6594	-7.04	-6.10
6554	2.120	2.120	6593	-7.12	-5.94
6562	2.130	2.130	6592	-7.23	-5.90
6569	2.140	2.140	6591	-7.34	-5.41
6577	2.150	2.150	6590	-7.48	-5.73
6584	2.160	2.160	6589	-7.48	-5.57
6592	2.170	2.170	6588	-6.81	-6.40
6599	2.180	2.180	6587	-6.87	-6.25
6607	2.190	2.190	6583	-6.92	-6.71
6614	2.200	2.200	6582	-7.20	-6.50
6637	2.230	2.230	6600	-7.09	-6.46
6645	2.240	2.240	7308	-7.69	-5.94
6652	2.250	2.250	9521	-7.37	-6.00
6660	2.260	2.260	6603	-7.58	-5.66
6667	2.270	2.270	9519	-7.71	-6.20
6675	2.280	2.280	9520	-7.61	-6.13
6682	2.290	2.290	9518	-7.73	-5.95
6690	2.300	2.300	6609	-7.05	-6.15
6697	2.310	2.310	7307	-7.86	-6.26
6705	2.320	2.320	4343	-7.60	-5.75
6720	2.340	2.340	7306	-7.17	-6.64
6730	2.354	2.354	7114	-6.86	-7.10
6732	2.356	2.356	7119	-6.64	-6.99
6738	2.364	2.364	7118	-7.62	-6.90
6739	2.366	2.366	7117	-7.38	-7.32
6746	2.374	2.374	7116	-7.33	-7.00
6747	2.376	2.376	7115	-7.59	-6.17
6753	2.384	2.384	7113	-6.85	-7.06
6753	2.384	2.384	7209	-7.11	-6.65
6755	2.386	2.386	7112	-6.91	-7.52
6758	2.390	2.390	7284	-7.23	-7.40
6758	2.390	2.390	6613	-7.42	-7.45
6761	2.394	2.394	7111	-6.70	-7.43
6762	2.396	2.396	7110	-6.85	-7.55
6765	2.400	2.400	4348	-7.04	-7.28
6768	2.404	2.404	7109	-7.34	-7.11
6770	2.406	2.406	7108	-7.03	-6.86
6773	2.410	2.410	4349	-6.42	-6.14
6776	2.414	2.414	7107	-6.78	-7.12
6777	2.416	2.416	7106	-6.30	-7.07
6780	2.420	2.420	4351	-6.15	-6.35
6783	2.424	2.424	7105	-7.02	-6.94
6785	2.426	2.426	7104	-7.25	-6.51
6788	2.430	2.430	7283	-7.07	-6.23
6806	2.454	2.454	7103	-7.31	-6.55
6807	2.456	2.456	7102	-7.34	-6.35
6810	2.460	2.460	7305	-7.71	-6.06

6813	2.464	2.464	7101	-7.81	-6.66
6813	2.464	2.464	7096	-7.79	-6.80
6821	2.474	2.474	7095	-7.17	-6.90
6822	2.476	2.476	7094	-6.98	-7.01
6825	2.480	2.480	7304	-6.92	-6.92
6827	2.482	2.482	7093	-6.85	-7.44
6828	2.484	2.484	7092	-6.64	-6.81
6830	2.486	2.486	7091	-6.96	-6.39
6833	2.490	2.490	6616	-7.05	-6.57
6836	2.494	2.494	7090	-7.12	-6.34
6837	2.496	2.496	7089	-6.43	-6.61
6840	2.500	2.500	7300	-7.37	-6.58
6843	2.504	2.504	7088	-7.70	-6.72
6845	2.506	2.506	7087	-7.64	-7.09
6848	2.510	2.510	6617	-7.64	-6.88
6851	2.514	2.514	7086	-7.49	-6.73
6852	2.516	2.516	7085	-7.54	-6.64
6855	2.520	2.520	4358	-7.85	-5.80
6858	2.524	2.524	7082	-7.52	-7.61
6860	2.526	2.526	7084	-7.69	-6.80
6863	2.530	2.530	4359	-7.23	-6.07
6866	2.534	2.534	7083	-6.94	-7.05
6868	2.536	2.536	7081	-7.08	-6.31
6871	2.540	2.540	6618	-7.05	-6.21
6874	2.544	2.544	7080	-7.00	-6.58
6875	2.546	2.546	7079	-6.71	-6.65
6878	2.550	2.550	6619	-7.13	-6.48
6881	2.554	2.554	7078	-6.05	-7.03
6883	2.556	2.556	7050	-6.42	-5.99
6886	2.560	2.560	6620	-6.63	-6.52
6890	2.566	2.566	6983	-6.75	-6.63
6893	2.570	2.570	6621	-6.68	-6.28
6896	2.574	2.574	6982	-6.65	-6.09
6898	2.576	2.576	6981	-7.12	-6.61
6901	2.580	2.580	7299	-7.33	-6.64
6904	2.584	2.584	6980	-7.03	-7.84
6905	2.586	2.586	6979	-7.13	-6.60
6908	2.590	2.590	7298	-7.09	-6.54
6911	2.594	2.594	6978	-7.70	-6.97
6913	2.596	2.596	6977	-7.69	-6.29
6916	2.600	2.600	12495	-7.00	-6.51
6919	2.604	2.604	6976	-7.22	-6.66
6920	2.606	2.606	7077	-7.33	-6.49
6923	2.610	2.610	7285	-7.05	-7.07
6926	2.614	2.614	7038	-7.22	-6.68
6928	2.616	2.616	7037	-7.00	-6.69
6931	2.620	2.620	6433	-7.10	-7.57
6935	2.626	2.626	7035	-6.74	-6.89
6938	2.630	2.630	6475	-6.81	-6.98
6946	2.640	2.640	7296	-6.91	-6.99

6953	2.650	2.650	6473	-7.03	-6.29
6961	2.660	2.660	6472	-6.79	-6.99
6964	2.664	2.664	6963	-6.89	-7.49
6965	2.666	2.666	7073	-6.90	-7.41
6968	2.670	2.670	6471	-6.53	-6.77
6970	2.672	2.672	7072	-7.36	-7.37
6971	2.674	2.674	7071	-6.82	-7.51
6973	2.676	2.676	7070	-7.14	-7.43
6976	2.680	2.680	6470	-6.94	-6.64
6979	2.684	2.684	7069	-6.93	-7.13
6980	2.686	2.686	7068	-7.00	-7.38
6984	2.690	2.690	6896	-6.98	-6.69
6987	2.694	2.694	7067	-6.93	-7.03
6988	2.696	2.696	7066	-6.61	-7.63
6991	2.700	2.700	7291	-6.67	-7.33
6994	2.704	2.704	6957	-6.42	-6.97
6996	2.706	2.706	6956	-6.54	-7.08
7002	2.714	2.714	6955	-6.53	-7.86
7003	2.716	2.716	7062	-6.91	-7.51
7006	2.720	2.720	6462	-6.85	-7.56
7009	2.724	2.724	7061	-6.83	-8.00
7011	2.726	2.726	7060	-7.08	-7.78
7017	2.734	2.734	7059	-7.01	-7.77
7018	2.736	2.736	7208	-6.88	-6.88
7021	2.740	2.740	6460	-7.39	-6.50
7024	2.744	2.744	7057	-6.77	-6.93
7026	2.746	2.746	7056	-6.61	-6.95
7029	2.750	2.750	7281	-7.09	-6.36
7032	2.754	2.754	7055	-7.35	-6.45
7033	2.756	2.756	7054	-7.08	-6.34
7036	2.760	2.760	6567	-7.27	-6.60
7044	2.770	2.770	7282	-6.78	-6.74
7051	2.780	2.780	7295	-7.33	-6.72
7059	2.790	2.790	6331	-7.22	-6.10
7066	2.800	2.800	6330	-7.62	-6.35
7074	2.810	2.810	6432	-8.14	-6.38
7074	2.810	2.810	6448	-8.22	-6.42
7081	2.820	2.820	6431	-7.32	-7.30
7089	2.830	2.830	6430	-6.97	-6.60
7096	2.840	2.840	6429	-6.84	-7.12
7104	2.850	2.850	6428	-7.03	-7.03
7112	2.860	2.860	6565	-6.81	-6.83
7119	2.870	2.870	6325	-6.81	-6.70
7127	2.880	2.880	7290	-6.74	-6.69
7134	2.890	2.890	6323	-6.90	-6.75
7134	2.890	2.890	7289	-7.04	-6.72
7142	2.900	2.900	6322	-6.50	-6.67
7149	2.910	2.910	6321	-7.21	-6.11
7157	2.920	2.920	6564	-6.71	-6.52
7164	2.930	2.930	6481	-6.85	-7.08

7172	2.940	2.940	6318	-7.12	-6.44
7179	2.950	2.950	6317	-7.13	-6.06
7187	2.960	2.960	6316	-7.63	-6.69
7194	2.970	2.970	6480	-7.56	-6.69
7194	2.970	2.970	7288	-7.54	-6.73
7202	2.980	2.980	7287	-8.08	-6.77
7209	2.990	2.990	6312	-7.74	-6.50
7217	3.000	3.000	7286	-7.92	-7.20
7240	3.030	3.030	2661	-7.86	-6.98
7247	3.040	3.040	2660	-7.32	-6.92
7255	3.050	3.050	2659	-7.10	-6.19
7262	3.060	3.060	12680	-7.47	-6.47
7270	3.070	3.070	2657	-7.67	-6.45
7277	3.080	3.080	12677	-6.74	-6.06
7285	3.090	3.090	2655	-6.51	-6.57
7292	3.100	3.100	2654	-6.88	-6.51
7300	3.110	3.110	2653	-6.77	-6.39
7315	3.130	3.130	12681	-7.86	-6.85
7322	3.140	3.140	2650	-7.98	-5.92
7330	3.150	3.150	2649	-7.63	-5.83
7337	3.160	3.160	2648	-7.51	-6.37
7345	3.170	3.170	2647	-7.71	-5.84
7353	3.180	3.180	12674	-8.14	-6.23
7360	3.190	3.190	2645	-7.73	-5.82
7375	3.210	3.210	2643	-7.81	-6.33
7383	3.220	3.220	2639	-7.23	-5.81
7390	3.230	3.230	2638	-7.80	-6.16
7398	3.240	3.240	2637	-7.51	-5.80
7405	3.250	3.250	2636	-7.43	-5.59
7413	3.260	3.260	2635	-7.62	-5.91
7420	3.270	3.270	2634	-7.28	-5.97
7428	3.280	3.280	2633	-7.36	-5.98
7435	3.290	3.290	2632	-6.73	-5.27
7443	3.300	3.300	2631	-6.57	-5.56
7450	3.310	3.310	2630	-7.54	-6.17
7458	3.320	3.320	2629	-7.52	-6.38
7466	3.330	3.330	2628	-7.73	-5.45
7473	3.340	3.340	2627	-7.37	-5.51
7481	3.350	3.350	2626	-7.41	-6.78
7488	3.360	3.360	2625	-7.24	-6.01
7496	3.370	3.370	2624	-7.02	-6.07
7503	3.380	3.380	2623	-7.36	-5.83
7511	3.390	3.390	2622	-6.89	-6.48
7518	3.400	3.400	2621	-6.94	-5.57
7526	3.410	3.410	2620	-7.27	-5.63
7533	3.420	3.420	2769	-7.90	-6.67
7541	3.430	3.430	2768	-7.59	-5.73
7548	3.440	3.440	2767	-7.47	-5.51
7556	3.450	3.450	2766	-7.70	-6.30
7563	3.460	3.460	2765	-7.59	-5.95

7571	3.470	3.470	2680	-7.87	-6.13
7579	3.480	3.480	12714	-8.54	-6.43
7586	3.490	3.490	2677	-7.70	-6.45
7594	3.500	3.500	2676	-6.99	-6.32
7601	3.510	3.510	2675	-7.88	-6.08
7609	3.520	3.520	2674	-7.26	-6.34
7616	3.530	3.530	2673	-7.06	-6.41
7624	3.540	3.540	2672	-7.33	-6.26
7631	3.550	3.550	2671	-7.19	-6.87
7638	3.560	3.560	2616	-6.86	-6.10
7643	3.570	3.570	2615	-7.21	-6.18
7649	3.580	3.580	2614	-7.22	-5.77
7654	3.590	3.590	2613	-7.56	-6.20
7660	3.600	3.600	2612	-7.38	-6.47
7665	3.610	3.610	12683	-7.72	-6.56
7671	3.620	3.620	2608	-6.97	-6.26
7676	3.630	3.630	2607	-6.89	-6.42
7682	3.640	3.640	2606	-6.73	-5.90
7687	3.650	3.650	2605	-7.61	-6.14
7693	3.660	3.660	2604	-7.06	-5.91
7698	3.670	3.670	2603	-6.68	-6.08
7703	3.680	3.680	2602	-6.79	-5.73
7709	3.690	3.690	2601	-5.94	-5.94
7714	3.700	3.700	2600	-6.44	-6.80
7720	3.710	3.710	2599	-6.79	-5.64
7725	3.720	3.720	2598	-6.55	-5.62
7731	3.730	3.730	2597	-6.55	-6.17
7736	3.740	3.740	2596	-6.84	-6.29
7742	3.750	3.750	2595	-6.84	-6.13
7747	3.760	3.760	12675	-7.16	-6.30
7748	3.762	3.762	12689	-6.98	-6.39
7753	3.770	3.770	2593	-7.10	-6.31
7758	3.780	3.780	2592	-6.88	-5.79
7764	3.790	3.790	2591	-6.50	-5.81
7769	3.800	3.800	2590	-5.86	-5.98
7775	3.810	3.810	2589	-6.64	-6.25
7780	3.820	3.820	2579	-6.43	-5.87
7786	3.830	3.830	2578	-7.66	-6.42
7791	3.840	3.840	12682	-7.77	-6.44
7797	3.850	3.850	2576	-7.85	-6.76
7802	3.860	3.860	12704	-7.07	-6.84
7813	3.880	3.880	12711	-7.06	-6.09
7819	3.890	3.890	12676	-7.32	-5.90
7830	3.910	3.910	12706	-7.09	-5.93
7835	3.920	3.920	2569	-6.63	-5.39
7840	3.930	3.930	2568	-7.07	-5.33
7846	3.940	3.940	2567	-6.80	-5.95
7851	3.950	3.950	12684	-7.24	-6.13
7857	3.960	3.960	2563	-6.86	-5.92
7862	3.970	3.970	12678	-6.99	-6.15

7868	3.980	3.980	2561	-7.14	-6.65
7873	3.990	3.990	2560	-7.55	-5.85
7879	4.000	4.000	2559	-7.14	-5.76
7895	4.030	4.030	2558	-7.56	-6.51
7901	4.040	4.040	2557	-6.62	-5.68
7906	4.050	4.050	2556	-6.73	-6.18
7912	4.060	4.060	2555	-6.85	-6.12
7917	4.070	4.070	2554	-6.78	-6.42
7923	4.080	4.080	2553	-6.77	-6.21
7928	4.090	4.090	2552	-7.34	-6.37
7934	4.100	4.100	2551	-7.07	-6.09
7945	4.120	4.120	2549	-7.15	-5.62
7950	4.130	4.130	12701	-8.07	-5.69
7956	4.140	4.140	12687	-7.36	-6.01
7961	4.150	4.150	12700	-7.53	-6.24
7967	4.160	4.160	12703	-7.48	-5.88
7972	4.170	4.170	12763	-7.37	-6.24
7977	4.180	4.180	2668	-7.28	-6.00
7983	4.190	4.190	2586	-6.92	-5.84
7988	4.200	4.200	12686	-7.71	-5.88
7994	4.210	4.210	2584	-6.76	-5.60
7999	4.220	4.220	2583	-6.85	-6.19
8005	4.230	4.230	2582	-6.77	-6.06
8010	4.240	4.240	2581	-6.75	-6.09
8016	4.250	4.250	2580	-7.32	-5.93
8021	4.260	4.260	2532	-6.22	-6.17
8027	4.270	4.270	2531	-6.65	-6.01
8032	4.280	4.280	12673	-6.92	-6.46
8038	4.290	4.290	2529	-6.48	-6.17
8043	4.300	4.300	12713	-6.63	-7.13
8049	4.310	4.310	12705	-6.19	-6.97
8054	4.320	4.320	2526	-5.88	-6.98
8060	4.330	4.330	12764	-6.20	-7.40
8065	4.340	4.340	12712	-6.63	-6.98
8071	4.350	4.350	12672	-6.79	-6.20
8076	4.360	4.360	12707	-6.85	-6.64
8082	4.370	4.370	2667	-6.51	-6.84
8087	4.380	4.380	2517	-6.37	-6.00
8093	4.390	4.390	2516	-6.17	-6.47
8098	4.400	4.400	2515	-5.80	-6.83
8100	4.404	4.404	13296	-5.96	-7.15
8104	4.410	4.410	2514	-7.04	-6.25
8106	4.414	4.414	13297	-7.15	-6.67
8109	4.420	4.420	2513	-6.16	-6.51
8111	4.424	4.424	13295	-6.23	-6.59
8114	4.430	4.430	2512	-5.96	-6.18
8117	4.434	4.434	13292	-6.54	-6.59
8120	4.440	4.440	2511	-6.27	-5.65
8122	4.444	4.444	13289	-6.89	-6.42
8125	4.450	4.450	2510	-5.68	-6.06

8128	4.454	4.454	12802	-6.70	-5.99
8131	4.460	4.460	2509	-6.53	-4.95
8133	4.464	4.464	12801	-7.24	-5.67
8136	4.470	4.470	2508	-6.91	-5.17
8139	4.474	4.474	12800	-6.81	-6.13
8142	4.480	4.480	2507	-6.62	-5.40
8144	4.484	4.484	12799	-7.02	-6.04
8147	4.490	4.490	2506	-6.74	-5.95
8150	4.494	4.494	13288	-6.45	-6.50
8153	4.500	4.500	2505	-6.38	-5.71
8155	4.504	4.504	13291	-6.82	-5.96
8158	4.510	4.510	2504	-6.31	-5.32
8164	4.520	4.520	2503	-6.69	-5.71
8169	4.530	4.530	2502	-6.50	-5.35
8175	4.540	4.540	2501	-6.22	-6.19
8180	4.550	4.550	2500	-6.45	-6.08
8186	4.560	4.560	2499	-6.60	-6.00
8191	4.570	4.570	2498	-6.41	-5.63
8193	4.574	4.574	12803	-7.32	-6.38
8197	4.580	4.580	12710	-6.96	-6.45
8199	4.584	4.584	12798	-7.05	-5.80
8202	4.590	4.590	2491	-7.38	-6.02
8204	4.594	4.594	12797	-6.94	-5.88
8208	4.600	4.600	2670	-6.88	-6.37
8213	4.610	4.610	2489	-7.10	-5.80
8219	4.620	4.620	2488	-7.12	-6.95
8221	4.624	4.624	12796	-6.44	-5.87
8224	4.630	4.630	2486	-7.68	-5.84
8226	4.634	4.634	12795	-7.47	-6.21
8230	4.640	4.640	2485	-7.45	-6.43
8232	4.644	4.644	13293	-6.76	-6.07
8235	4.650	4.650	2484	-6.53	-5.61
8237	4.654	4.654	13290	-6.61	-6.02
8240	4.660	4.660	2483	-6.21	-5.58
8243	4.664	4.664	13287	-6.13	-5.80
8246	4.670	4.670	2482	-5.92	-5.40
8248	4.674	4.674	13278	-5.94	-5.83
8251	4.680	4.680	2481	-5.86	-5.53
8254	4.684	4.684	13283	-6.83	-6.04
8257	4.690	4.690	2480	-6.99	-5.92
8259	4.694	4.694	13279	-7.19	-6.52
8262	4.700	4.700	2479	-7.16	-5.93
8265	4.704	4.704	12794	-7.05	-6.27
8268	4.710	4.710	2478	-7.39	-6.34
8270	4.714	4.714	13282	-6.36	-6.63
8273	4.720	4.720	2477	-6.62	-5.80
8276	4.724	4.724	12793	-7.21	-5.82
8279	4.730	4.730	2476	-7.07	-5.91
8281	4.734	4.734	12804	-7.42	-6.35
8284	4.740	4.740	2475	-7.50	-5.91

8287	4.744	4.744	13281	-7.02	-6.22
8290	4.750	4.750	2474	-7.00	-5.73
8292	4.754	4.754	13294	-8.18	-5.75
8295	4.760	4.760	2473	-7.30	-5.52
8297	4.764	4.764	12778	-7.00	-6.34
8297	4.764	4.764	13280	-6.61	-6.28
8301	4.770	4.770	2472	-6.62	-6.34
8303	4.774	4.774	12791	-6.99	-6.45
8306	4.780	4.780	2669	-7.07	-6.48
8308	4.784	4.784	12790	-7.01	-6.70
8312	4.790	4.790	2470	-7.01	-6.64
8314	4.794	4.794	12785	-6.68	-6.80
8315	4.796	4.796	9516	-5.47	-7.04
8316	4.798	4.798	9517	-6.87	-6.50
8323	4.810	4.810	2469	-6.74	-5.92
8325	4.814	4.814	12786	-7.48	-6.76
8330	4.824	4.824	12781	-6.95	-6.20
8334	4.830	4.830	2467	-6.95	-6.51
8336	4.834	4.834	12789	-5.88	-6.63
8339	4.840	4.840	12688	-6.54	-6.35
8341	4.844	4.844	12788	-4.91	-6.85
8345	4.850	4.850	12690	-6.50	-6.24
8347	4.854	4.854	12779	-6.44	-6.25
8350	4.860	4.860	12512	-6.03	-6.37
8352	4.864	4.864	12787	-5.57	-6.96
8356	4.870	4.870	2460	-5.92	-5.98
8358	4.874	4.874	12780	-6.26	-6.53
8361	4.880	4.880	2459	-6.48	-6.49
8367	4.890	4.890	2458	-6.58	-6.21
8372	4.900	4.900	2457	-7.11	-6.15
8377	4.910	4.910	2456	-6.60	-6.47
8383	4.920	4.920	2455	-6.57	-6.45
8388	4.930	4.930	2454	-6.03	-5.97
8394	4.940	4.940	2453	-5.92	-6.89
8399	4.950	4.950	2452	-6.00	-6.03
8405	4.960	4.960	2451	-6.35	-6.07
8410	4.970	4.970	2450	-5.68	-5.93
8427	4.980	4.980	2449	-5.70	-6.60
8449	4.990	4.990	2448	-5.80	-6.16
8470	5.000	5.000	2447	-5.90	-6.19
8492	5.010	5.010	2446	-5.50	-6.36
8505	5.016	5.016	9507	-7.04	-6.34
8513	5.020	5.020	2445	-6.98	-5.78
8535	5.030	5.030	2444	-7.01	-5.77
8556	5.040	5.040	2440	-6.25	-6.08
8578	5.050	5.050	2439	-6.08	-6.15
8599	5.060	5.060	2438	-6.01	-6.29
8621	5.070	5.070	2437	-5.99	-6.04
8643	5.080	5.080	2436	-6.39	-6.82
8664	5.090	5.090	2435	-6.29	-6.40

8686	5.100	5.100	2434	-6.64	-6.14
8707	5.110	5.110	2433	-6.13	-6.23
8729	5.120	5.120	2432	-5.89	-6.04
8750	5.130	5.130	2431	-5.44	-6.40
8772	5.140	5.140	2430	-6.05	-5.73
8793	5.150	5.150	2429	-5.72	-6.43
8815	5.160	5.160	2428	-5.61	-6.08
8836	5.170	5.170	2427	-5.35	-6.73
8858	5.180	5.180	2426	-5.43	-6.36
8880	5.190	5.190	2425	-5.65	-6.09
8901	5.200	5.200	2424	-5.23	-6.59
8923	5.210	5.210	2423	-5.45	-6.14
8944	5.220	5.220	2422	-5.21	-5.69
8966	5.230	5.230	2421	-5.97	-6.49
8987	5.240	5.240	2409	-5.72	-6.74
9009	5.250	5.250	2408	-5.60	-6.80
9030	5.260	5.260	2407	-5.53	-5.94
9052	5.270	5.270	2406	-5.56	-6.04
9074	5.280	5.280	2405	-5.78	-6.42
9095	5.290	5.290	2404	-5.83	-5.92
9117	5.300	5.300	2403	-6.18	-5.62
9138	5.310	5.310	2402	-6.17	-5.87
9160	5.320	5.320	2399	-5.86	-5.74
9181	5.330	5.330	2398	-5.99	-5.89
9203	5.340	5.340	2397	-5.92	-5.74
9224	5.350	5.350	2396	-6.00	-5.94
9246	5.360	5.360	2395	-6.17	-6.05
9267	5.370	5.370	2243	-5.83	-5.52
9289	5.380	5.380	2242	-6.30	-5.93
9311	5.390	5.390	2241	-5.69	-5.80
9332	5.400	5.400	2240	-5.75	-5.54
9354	5.410	5.410	2239	-5.78	-6.20
9375	5.420	5.420	2238	-5.46	-5.94
9397	5.430	5.430	2237	-6.41	-5.51
9418	5.440	5.440	2233	-5.72	-5.53
9440	5.450	5.450	2232	-5.75	-5.17
9461	5.460	5.460	2231	-5.73	-5.59
9483	5.470	5.470	2230	-5.97	-5.55
9504	5.480	5.480	2229	-5.71	-5.57
9526	5.490	5.490	2228	-5.57	-5.83
9548	5.500	5.500	2227	-5.44	-5.96
9569	5.510	5.510	2226	-5.52	-5.44
9591	5.520	5.520	2225	-5.63	-5.50
9612	5.530	5.530	2224	-6.04	-5.43
9634	5.540	5.540	2223	-5.69	-6.11
9655	5.550	5.550	2222	-5.88	-6.44
9677	5.560	5.560	2221	-5.57	-5.73
9698	5.570	5.570	2220	-5.76	-6.29
9720	5.580	5.580	2219	-5.84	-5.81
9742	5.590	5.590	2218	-6.17	-5.53

9763	5.600	5.600	2217	-6.71	-5.67
9785	5.610	5.610	2216	-5.46	-5.75
9806	5.620	5.620	2215	-5.47	-5.79
9828	5.630	5.630	2214	-5.27	-5.35
9849	5.640	5.640	2497	-5.50	-5.30
9871	5.650	5.650	2496	-5.70	-5.04
9892	5.660	5.660	2540	-5.42	-5.28
9914	5.670	5.670	2539	-5.39	-5.46
9935	5.680	5.680	12570	-5.44	-5.99
9935	5.680	5.680	12771	-5.27	-5.97
9957	5.690	5.690	2537	-5.57	-5.19
9979	5.700	5.700	2536	-5.14	-5.35
10000	5.710	5.710	2535	-4.29	-5.59
10022	5.720	5.720	12514	-5.19	-6.22
10043	5.730	5.730	2105	-5.04	-4.77
10060	5.738	5.738	2104	-4.91	-4.92
10086	5.750	5.750	2103	-4.69	-4.76
10108	5.760	5.760	2102	-5.11	-5.07
10129	5.770	5.770	2101	-5.15	-4.57
10151	5.780	5.780	2100	-4.90	-5.16
10172	5.790	5.790	2099	-5.03	-4.42
10194	5.800	5.800	2098	-4.83	-4.79
10216	5.810	5.810	2097	-4.47	-5.18
10237	5.820	5.820	2096	-4.37	-5.87
10259	5.830	5.830	2092	-4.04	-4.94
10280	5.840	5.840	2091	-4.25	-5.15
10302	5.850	5.850	2090	-3.98	-4.86
10323	5.860	5.860	2089	-3.62	-5.63
10345	5.870	5.870	2088	-3.49	-4.75
10366	5.880	5.880	2087	-3.68	-5.11
10388	5.890	5.890	2086	-3.76	-5.46
10410	5.900	5.900	2085	-4.01	-5.42
10431	5.910	5.910	2084	-3.88	-4.79
10453	5.920	5.920	2083	-4.34	-4.29
10474	5.930	5.930	2082	-4.14	-4.66
10496	5.940	5.940	2081	-3.84	-5.01
10517	5.950	5.950	2080	-3.61	-5.69
10539	5.960	5.960	2079	-3.58	-5.15
10560	5.970	5.970	2120	-3.91	-6.31
10582	5.980	5.980	2076	-3.71	-5.78
10603	5.990	5.990	2075	-4.20	-6.18
10625	6.000	6.000	2074	-3.83	-6.07
10677	6.024	6.024	1459	-3.12	-5.74
10698	6.034	6.034	1460	-2.58	-6.02
10711	6.040	6.040	1319	-3.60	-6.67
10720	6.044	6.044	1461	-2.08	-5.90
10733	6.050	6.050	1318	-2.44	-6.78
10741	6.054	6.054	1462	-2.87	-5.95
10754	6.060	6.060	1317	-2.68	-6.69
10763	6.064	6.064	12511	-2.31	-6.80

10776	6.070	6.070	12507	-3.22	-6.59
10784	6.074	6.074	12518	-3.51	-6.47
10797	6.080	6.080	1315	-2.49	-6.60
10806	6.084	6.084	1465	-2.88	-6.24
10819	6.090	6.090	1314	-2.94	-6.25
10828	6.094	6.094	1466	-2.94	-6.45
10840	6.100	6.100	1456	-3.96	-6.27
10849	6.104	6.104	1467	-3.22	-6.06
10862	6.110	6.110	1457	-2.99	-5.81
10884	6.120	6.120	1308	-1.72	-6.88
10905	6.130	6.130	1458	-1.82	-6.53
10927	6.140	6.140	1306	-1.62	-6.40
10948	6.150	6.150	1305	-1.36	-6.45
10970	6.160	6.160	1304	-1.60	-6.61
10991	6.170	6.170	1301	-1.61	-5.86
11013	6.180	6.180	1300	-1.66	-5.48
11034	6.190	6.190	1299	-1.24	-6.70
11056	6.200	6.200	1297	-0.99	-6.13
11077	6.210	6.210	1295	-1.26	-5.41
11099	6.220	6.220	1294	-1.57	-6.31
11121	6.230	6.230	1293	-0.85	-7.18
11142	6.240	6.240	1287	-1.30	-6.70
11159	6.248	6.248	9515	-1.55	-6.26
11164	6.250	6.250	12505	-1.44	-6.30
11179	6.260	6.260	1285	-2.02	-6.70
11192	6.270	6.270	12508	-1.16	-7.24
11205	6.280	6.280	1283	-1.59	-6.22
11219	6.290	6.290	1282	-1.59	-6.28
11232	6.300	6.300	1281	-1.42	-6.18
11232	6.300	6.300	1328	-1.39	-6.35
11237	6.304	6.304	1389	-1.80	-5.73
11245	6.310	6.310	1280	-1.82	-5.53
11251	6.314	6.314	1390	-1.70	-5.66
11259	6.320	6.320	1279	-1.65	-6.25
11264	6.324	6.324	1391	-1.52	-5.40
11270	6.328	6.328	1392	-1.68	-5.56
11272	6.330	6.330	1278	-1.73	-6.21
11278	6.334	6.334	1393	-1.80	-5.98
11283	6.338	6.338	1394	-1.55	-5.96
11286	6.340	6.340	1277	-2.74	-6.67
11291	6.344	6.344	1395	-1.64	-6.01
11296	6.348	6.348	1396	-0.77	-5.84
11299	6.350	6.350	1276	-0.53	-5.36
11304	6.354	6.354	1397	-0.83	-5.18
11310	6.358	6.358	1398	-0.69	-5.27
11312	6.360	6.360	1275	-0.64	-5.85
11318	6.364	6.364	1399	-0.88	-5.37
11323	6.368	6.368	1400	-0.86	-5.09
11326	6.370	6.370	1271	-0.82	-6.04
11331	6.374	6.374	1401	-0.59	-5.95

11336	6.378	6.378	12510	-0.90	-5.89
11339	6.380	6.380	1270	-0.63	-6.06
11344	6.384	6.384	12572	-0.49	-6.42
11350	6.388	6.388	12560	-0.17	-6.21
11350	6.388	6.388	12663	-0.24	-6.20
11352	6.390	6.390	1269	-0.52	-6.58
11358	6.394	6.394	12567	-0.09	-6.85
11358	6.394	6.394	12767	0.02	-6.56
11363	6.398	6.398	12517	0.29	-6.20
11366	6.400	6.400	1268	0.35	-6.59
11371	6.404	6.404	12509	0.79	-6.11
11376	6.408	6.408	12519	1.31	-6.54
11379	6.410	6.410	1267	0.23	-6.86
11390	6.418	6.418	12524	0.77	-6.32
11392	6.420	6.420	1422	0.11	-5.79
11400	6.426	6.426	1423	-2.28	-6.37
11403	6.428	6.428	12496	-2.64	-7.53
11406	6.430	6.430	1424	0.23	-7.28
11408	6.432	6.432	12497	0.26	-6.40
11408	6.432	6.432	12708	-0.40	-6.22
11411	6.434	6.434	7313	-1.05	-6.19
11419	6.440	6.440	1426	-0.52	-8.21
11614	6.586	6.586	7319	1.82	-7.29
11617	6.588	6.588	7317	1.49	-6.80
11619	6.590	6.590	1208	-0.71	-5.66
11633	6.600	6.600	1207	-1.47	-5.14
11646	6.610	6.610	1206	-1.26	-6.02
11659	6.620	6.620	1303	-1.43	-5.69
11673	6.630	6.630	1302	-1.45	-5.77
11684	6.638	6.638	12709	-1.29	-6.24
11686	6.640	6.640	12576	-1.75	-6.07
11686	6.640	6.640	12777	-1.89	-6.11
11686	6.640	6.640	13299	-1.28	-5.75
11692	6.644	6.644	12575	-1.56	-5.86
11697	6.648	6.648	12569	-1.90	-5.21
11697	6.648	6.648	12770	-1.81	-5.10
11700	6.650	6.650	12568	-1.90	-5.75
11700	6.650	6.650	12768	-1.90	-5.50
11705	6.654	6.654	12564	-1.79	-5.94
11705	6.654	6.654	12667	-1.74	-5.76
11710	6.658	6.658	12559	-1.66	-6.33
11710	6.658	6.658	12662	-1.61	-5.98
11713	6.660	6.660	12573	-1.71	-6.31
11718	6.664	6.664	12561	-0.90	-5.33
11718	6.664	6.664	12664	-0.87	-5.24
11724	6.668	6.668	12554	-1.42	-5.86
11724	6.668	6.668	12660	-1.02	-5.54
11726	6.670	6.670	12516	-1.17	-5.97
11732	6.674	6.674	12523	-1.00	-5.80
11740	6.680	6.680	12558	-1.37	-6.44

11740	6.680	6.680	12661	-1.29	-6.21
11745	6.684	6.684	12562	-1.95	-6.59
11745	6.684	6.684	12665	-1.91	-6.48
11753	6.690	6.690	12515	-1.29	-6.25
11758	6.694	6.694	12563	-1.84	-6.51
11758	6.694	6.694	12666	-1.86	-6.23
11766	6.700	6.700	12571	-1.62	-6.10
11781	6.704	6.704	12574	-1.17	-6.38
11816	6.710	6.710	1296	-1.59	-6.68
11875	6.720	6.720	12520	-1.13	-5.72
11933	6.730	6.730	12513	-1.08	-6.40
11992	6.740	6.740	12506	-1.07	-6.31
12051	6.750	6.750	1292	-1.29	-6.37
12074	6.754	6.754	12565	-1.49	-6.27
12110	6.760	6.760	12522	-0.80	-6.05
12133	6.764	6.764	12766	-0.72	-6.23
12168	6.770	6.770	12521	-0.77	-5.76
12227	6.780	6.780	965	-0.96	-5.55
12286	6.790	6.790	964	-1.16	-5.92
12345	6.800	6.800	963	-0.90	-5.98
12403	6.810	6.810	962	-2.20	-5.60
12462	6.820	6.820	961	-1.14	-5.83
12521	6.830	6.830	960	-1.07	-5.66
12580	6.840	6.840	959	-2.58	-5.94
12638	6.850	6.850	958	-2.41	-6.31
12697	6.860	6.860	957	-1.22	-5.07
12756	6.870	6.870	956	-1.01	-5.04
12814	6.880	6.880	955	-1.17	-5.53
12932	6.900	6.900	953	-0.57	-5.66
12991	6.910	6.910	952	-0.74	-5.53
13049	6.920	6.920	951	-0.88	-5.85
13108	6.930	6.930	950	-0.84	-5.58
13167	6.940	6.940	949	-0.69	-5.82
13226	6.950	6.950	948	-0.48	-5.55
13284	6.960	6.960	947	0.05	-5.93
13343	6.970	6.970	946	0.12	-5.83
13402	6.980	6.980	945	-0.02	-5.75
13519	7.000	7.000	943	-0.81	-5.97
13578	7.010	7.210	926	-1.05	-5.95
13637	7.020	7.220	831	-0.42	-5.81
13695	7.030	7.230	832	0.25	-5.18
13754	7.040	7.240	833	0.00	-5.13
13813	7.050	7.250	834	0.53	-4.95
13872	7.060	7.260	835	0.12	-5.42
13930	7.070	7.270	836	0.32	-4.72
13989	7.080	7.280	837	0.35	-4.94
14048	7.090	7.290	838	0.31	-5.13
14107	7.100	7.300	839	0.62	-5.86
14165	7.110	7.310	840	0.36	-5.17
14224	7.120	7.320	841	0.49	-5.42

14283	7.130	7.330	842	0.37	-5.54
14342	7.140	7.340	843	0.30	-6.06
14400	7.150	7.350	844	0.90	-5.67
14459	7.160	7.360	845	1.06	-5.35
14518	7.170	7.370	846	1.07	-5.15
14576	7.180	7.380	847	1.24	-6.34
14635	7.190	7.390	848	0.74	-5.76
14694	7.200	7.400	849	1.54	-6.31
14753	7.210	7.410	850	0.40	-6.08
14811	7.220	7.420	851	0.72	-6.38
14870	7.230	7.430	852	1.51	-6.29
14929	7.240	7.440	853	1.52	-5.76
14988	7.250	7.450	854	1.12	-5.44
15046	7.260	7.460	855	1.27	-5.42
15105	7.270	7.470	856	1.66	-5.21
15164	7.280	7.480	857	1.46	-5.51
15223	7.290	7.490	858	2.03	-5.62
15281	7.300	7.500	859	1.23	-5.32
15340	7.310	7.510	860	1.47	-5.25
15399	7.320	7.520	861	1.48	-5.32
15457	7.330	7.530	862	1.78	-5.17
15516	7.340	7.540	863	1.75	-5.19
15575	7.350	7.550	864	2.03	-5.20
15634	7.360	7.560	865	1.82	-6.14
15692	7.370	7.570	866	2.34	-5.52
15751	7.380	7.580	867	2.08	-5.80
15869	7.400	7.600	927	1.99	-6.24
15927	7.410	7.610	928	1.76	-5.83
15986	7.420	7.620	929	1.86	-6.15
16045	7.430	7.630	930	2.30	-5.51
16104	7.440	7.640	931	2.40	-5.26
16162	7.450	7.650	932	2.46	-5.48
16221	7.460	7.660	933	1.46	-5.84
16280	7.470	7.670	934	2.30	-4.96
16303	7.474	7.674	1468	1.07	-5.71
16338	7.480	7.680	935	1.07	-5.42
16362	7.484	7.684	1469	2.01	-5.00
16397	7.490	7.690	936	2.23	-5.51
16421	7.494	7.694	1470	2.57	-5.66
16456	7.500	7.700	937	2.67	-6.45
16479	7.504	7.704	1471	2.67	-5.85
16515	7.510	7.710	938	2.48	-6.34
16538	7.514	7.714	1472	2.67	-6.99
16573	7.520	7.720	939	2.14	-7.03
16597	7.524	7.724	1473	2.41	-6.87
16632	7.530	7.730	940	2.53	-7.59
16656	7.534	7.734	2072	2.42	-6.70
16691	7.540	7.740	941	2.55	-7.36
16714	7.544	7.744	2073	2.53	-7.04

APPENDIX D. CARBON AND OXYGEN STABLE ISOTOPE VALUES OF LINC-PC1 BULK CALCITE

Depth (m)	Saskatchewan Laboratory Number	$\delta^{13}C$ ‰ VPDB	$\delta^{18}O$ ‰ VPDB
0.010	7121	-6.61	-5.82
0.012	7267	-6.29	-5.87
0.014	7268	-6.52	-5.93
0.016	7269	-6.42	-5.90
0.018	7270	-6.37	-5.89
0.020	7122	-6.66	-5.87
0.022	7271	-6.46	-6.01
0.026	7273	-6.53	-6.23
0.028	7324	-6.10	-5.43
0.030	7123	-6.30	-6.03
0.034	7327	-6.01	-5.73
0.036	7328	-6.26	-5.85
0.038	7329	-6.47	-5.94
0.040	7124	-6.19	-5.93
0.040	7333	-6.37	-5.59
0.042	7330	-6.06	-5.73
0.044	7331	-6.08	-5.36
0.046	7332	-6.72	-5.24
0.050	7125	-5.98	-6.09
0.054	7335	-6.00	-5.58
0.056	7373	-6.17	-6.05
0.058	7337	-6.10	-5.81
0.060	7126	-6.30	-5.98
0.062	7338	-6.16	-5.62
0.066	7340	-6.40	-5.51
0.068	7341	-6.39	-5.21
0.070	7127	-6.43	-5.91
0.072	7342	-6.35	-5.52
0.074	7343	-6.39	-5.92
0.076	7344	-6.70	-5.23
0.078	7348	-6.08	-5.12
0.080	7128	-6.33	-5.92
0.082	7349	-6.61	-5.27
0.088	7381	-6.87	-6.04
0.090	7129	-6.19	-5.86
0.092	7382	-6.30	-5.39
0.094	7383	-6.44	-5.97
0.096	7384	-6.90	-5.54

0.098	7385	-6.50	-5.36
0.100	7137	-6.50	-5.77
0.100	7210	-6.05	-5.70
0.102	7386	-6.57	-5.41
0.104	7387	-6.30	-5.69
0.106	7388	-6.57	-5.61
0.108	7389	-6.59	-5.86
0.110	7138	-6.42	-5.89
0.110	7211	-6.34	-5.59
0.120	7212	-6.65	-5.73
0.130	7213	-5.67	-5.60
0.140	7214	-5.80	-5.61
0.150	7215	-5.65	-6.03
0.160	7216	-5.89	-5.89
0.170	7217	-5.81	-5.85
0.180	7153	-5.41	-6.04
0.190	7154	-5.72	-5.70
0.200	7156	-5.89	-5.81
0.210	7218	-5.76	-5.87
0.220	7200	-6.17	-5.73
0.230	7201	-5.92	-5.90
0.240	7202	-5.34	-5.98
0.250	7203	-7.03	-5.33
0.260	7204	-5.94	-5.75
0.270	7147	-5.98	-5.81
0.280	7148	-5.80	-5.63
0.290	7149	-5.68	-6.10
0.300	7219	-6.57	-5.76
0.310	7220	-6.24	-5.75
0.320	7221	-6.23	-5.57
0.330	7222	-6.03	-5.87
0.340	7223	-5.83	-5.83
0.350	7224	-5.85	-5.88
0.360	7225	-5.87	-5.57
0.370	7226	-6.00	-5.55
0.380	7231	-5.76	-5.57
0.390	7232	-5.83	-5.34
0.400	7233	-5.13	-5.74
0.410	7234	-4.66	-5.93
0.420	7235	-5.11	-5.58
0.430	7236	-5.23	-5.13
0.440	7237	-5.28	-5.63
0.450	7238	-5.24	-5.16

0.460	7239	-5.64	-5.24
0.470	7240	-4.59	-5.67
0.480	7241	-4.65	-5.01
0.490	7242	-4.14	-5.36
0.500	7243	-4.53	-5.15
0.510	7244	-4.69	-5.41
0.530	7245	-4.64	-5.13
0.540	7246	-4.86	-5.14
0.550	7247	-4.69	-6.33
0.560	7248	-4.62	-5.62
0.570	7249	-4.80	-5.56
0.580	7250	-3.73	-5.35
0.590	7254	-4.74	-5.22
0.600	7255	-5.16	-5.78
0.610	7256	-5.59	-5.26
0.620	7257	-3.80	-5.29
0.630	7258	-3.71	-4.68
0.640	7259	-3.76	-4.74
0.650	7260	-3.95	-5.01
0.660	7261	-3.05	-5.16
0.670	7262	-3.36	-5.30
0.680	7263	-3.93	-5.31
0.690	7264	-2.92	-5.23
0.700	7265	-2.73	-5.15
0.710	7266	-2.95	-5.20

APPENDIX E. ELEMENTAL ANALYSES AND CARBON AND NITROGEN STABLE ISOTOPE VALUES OF LINC-1.

Cal. Yr B.P.	Depth (m)	Depth (m, uncorrected)	$\delta^{13}C_{org}$ ‰ VPDB	%C	TOC	$\delta^{15}N$ ‰ AIR	%N	TN	C/N ratio	C/N ratio (N corrected)	$\Delta\delta^{13}C_{calcite - org}$
n.a.	0.030	0.030	-29.1	47.4	10.2	4.2	3.0	0.6	18.5	19.9	23.7
n.a.	0.050	0.050	-29.2	46.4	11.0	3.8	3.1	0.7	17.6	18.8	23.7
n.a.	0.144	0.144	-31.7	39.6	4.3	0.3	2.7	0.3	17.1	20.3	27.3
n.a.	0.250	0.250	-28.9	44.5	7.1	4.7	2.9	0.5	17.9	19.9	28.9
5536	1.060	1.060	-32.9	46.4	3.4	1.2	3.4	0.2	15.7	19.3	23.7
5586	1.100	1.100	-32.7	41.8		0.9	3.1		15.5		24.9
5649	1.150	1.150	-33.8	44.6	10.3	0.9	3.1	0.7	16.7	17.8	26.2
5711	1.200	1.200	-33.8	41.8	8.0	1.1	3.1	0.6	15.9	17.3	26.4
5773	1.250	1.250	-34.6	41.9	5.6	0.6	3.0	0.4	16.2	18.3	28.0
5773	1.250	1.250	-34.5	39.1	5.3	0.6	2.8	0.4	16.2	18.5	34.5
5836	1.300	1.300	-33.3	41.5	2.5		3.1	0.2	15.6	20.8	26.8
5898	1.350	1.350	-33.3	41.3	5.2	0.9	3.1	0.4	15.3	17.4	25.9
5923	1.370	1.370	-32.0	37.9	5.7	0.7	3.1	0.5	14.0	15.5	24.3
5961	1.400	1.400	-31.8	40.3	9.3	0.8	3.2	0.7	14.5	15.4	31.8
6073	1.490	1.490	-31.5	38.1	4.0	1.0	3.3	0.4	13.3	15.3	25.0
6125	1.550	1.550	-30.9	34.9	4.1	0.5	2.9	0.3	14.0	16.2	24.0
6163	1.600	1.600	-32.0	35.9		0.4	2.9		14.4		24.9
6199	1.648	1.648	-32.9	33.0	4.4	0.5	2.7	0.4	14.3	16.4	25.6
6236	1.698	1.698	-32.4	37.5	8.4	0.1	3.3	0.7	13.3	14.2	25.7
6274	1.748	1.748	-31.4	35.3	6.8	1.0	2.9	0.6	14.2	15.4	24.0
6313	1.800	1.800	-30.8	35.8	4.3	0.9	3.2	0.4	13.1	14.9	23.6
6351	1.850	1.850	-31.5	28.4	2.7	0.8	2.6	0.2	13.0	16.0	24.7
6387	1.898	1.898	-32.5	36.9	5.8	0.9	3.1	0.5	13.7	15.2	25.4
6404	1.920	1.920	-31.0	38.0	3.6	1.6	3.0	0.3	14.6	17.4	23.5
6425	1.948	1.948	-32.7	34.7	4.8	0.8	3.0	0.4	13.7	15.5	25.2
6434	1.960	1.960	-31.1	37.1	2.6	1.3	3.1	0.2	13.9	17.6	24.1
6462	1.998	1.998	-29.7	39.8		1.3	3.0		15.6		23.0
6539	2.100	2.100	-31.2	42.7		1.5	2.8		17.8		24.4
6574	2.146	2.146	-30.0	45.0	5.6	1.6	2.7	0.3	19.8	23.0	22.7
6607	2.190	2.190	-32.2	36.3	3.6	1.4	3.2	0.3	13.3	15.6	25.3

6652	2.250	2.250	-30.5	36.3		0.7	3.1		13.8		23.1
6690	2.300	2.300	-30.9	35.1	3.0	1.1	3.0	0.3	13.4	16.3	23.8
6727	2.350	2.350	-30.1	37.0	2.3	0.4	3.5	0.2	12.3	15.7	23.2
6765	2.400	2.400	-29.7	28.7	1.3	-0.2	2.6	0.1	13.0	21.2	22.7
6788	2.430	2.430	-30.8	31.7		1.2	2.9		12.6		23.8
6803	2.450	2.450	-32.0	35.5	1.8	0.4	3.2	0.2	13.1	18.2	24.7
6825	2.480	2.480	-32.0	34.5		0.7	3.0		13.3		25.1
6840	2.500	2.500	-33.0	37.8	4.4	0.1	2.9	0.3	15.2	17.6	25.6
6855	2.520	2.520	-32.8	35.8	7.1	0.5	3.0	0.6	14.0	15.2	25.0
6871	2.540	2.540	-33.5	35.3		0.7	2.9		14.1		26.4
6893	2.570	2.570	-34.0	36.2		0.8	2.8		15.2		27.3
6908	2.590	2.590	-32.5	38.5	6.7	0.5	2.9	0.5	15.5	17.0	25.4
6931	2.620	2.620	-32.4	39.6		0.3	3.3		14.2		25.3
6953	2.650	2.650	-31.6	38.1		0.2	3.5		12.5		24.6
6976	2.680	2.680	-31.4	38.1		0.2	3.5		12.8		24.4
6991	2.700	2.700	-30.3	43.8	3.7	0.4	3.5	0.3	14.7	17.4	23.6
7021	2.740	2.740	-30.9	41.4	3.0	0.1	3.5	0.3	13.7	16.7	23.5
7036	2.760	2.760	-30.4	38.0	2.9	0.0	3.3	0.3	13.3	16.4	23.2
7059	2.790	2.790	-30.8	29.6	3.1	0.6	2.7	0.3	12.9	15.5	23.6
7096	2.840	2.840	-30.5	28.4	2.5	0.2	2.6	0.2	12.5	15.7	23.6
7134	2.890	2.890	-30.9	31.7	4.6	0.8	2.8	0.4	13.3	15.0	24.0
7164	2.930	2.930	-30.9	35.2	2.9	1.6	3.0	0.2	13.9	17.1	23.8
7179	2.950	2.950	-30.7	32.8	2.2	-0.1	2.9	0.2	13.1	17.1	23.5
7194	2.970	2.970	-31.2	32.9	1.9	1.3	2.8	0.2	13.5	18.6	23.6
7209	2.990	2.990	-31.2	29.0	3.7	1.3	2.6	0.3	13.0	15.1	23.7
7255	3.050	3.050	-31.1	32.1	2.9	0.2	2.8	0.3	13.6	16.7	24.0
7277	3.080	3.080	-31.0	37.2	2.4	1.0	3.3	0.2	13.4	17.1	24.3
7292	3.100	3.100	-30.5	30.8	3.9	0.4	2.7	0.3	13.1	15.1	23.6
7300	3.110	3.110	-31.1	28.9	2.1	1.2	2.5	0.2	13.3	17.6	24.3
7307	3.120	3.120	-31.2	28.3	2.9	1.7	2.6	0.3	12.6	15.3	31.2
7330	3.150	3.150	-30.7	34.1	3.4	0.5	3.0	0.3	13.1	15.5	23.1
7368	3.200	3.200	-30.6	34.5	3.1	1.0	3.2	0.3	12.5	14.9	30.6
7405	3.250	3.250	-30.7	40.4	3.1	0.7	3.5	0.3	13.4	16.2	23.3
7443	3.300	3.300	-31.4	39.2	4.6	1.4	3.1	0.4	14.7	16.8	24.8
7458	3.320	3.320	-30.7	45.8		2.4	3.4		15.5		23.2
7466	3.330	3.330	-31.1	42.4		1.7	3.4		14.4		23.4

7481	3.350	3.350	-32.7	40.0	2.5	1.0	3.4	0.2	13.8	17.6	25.2
7488	3.360	3.360	-31.8	42.5	2.7	1.6	3.6	0.2	13.6	17.1	24.5
7496	3.370	3.370	-31.7	41.7	2.1	1.6	3.6	0.2	13.5	18.1	24.7
7518	3.400	3.400	-31.9	41.8	5.3	0.6	3.6	0.5	13.5	15.1	25.0
7556	3.450	3.450	-31.0	39.7	3.6	1.3	3.4	0.3	13.7	16.2	23.3
7609	3.520	3.520	-31.6	37.9	3.5	0.8	3.3	0.3	13.5	15.9	24.4
7624	3.540	3.540	-30.9	38.4	2.6	0.7	3.3	0.2	13.5	17.0	23.6
7665	3.610	3.610	-31.0	35.4	3.9	0.6	3.1	0.3	13.4	15.5	23.3
7698	3.670	3.670	-30.1	38.3	2.7	0.8	3.4	0.2	13.2	16.4	23.4
7720	3.710	3.710	-30.3	37.3	3.1	0.5	3.3	0.3	13.4	16.1	23.5
7747	3.760	3.760	-30.3	35.3	2.5	0.7	3.0	0.2	13.9	17.9	23.2
7775	3.810	3.810	-30.7	33.7	2.7	0.7	2.9	0.2	13.6	16.9	24.0
7802	3.860	3.860	-30.8	38.1	3.3	0.8	3.1	0.3	14.4	17.4	23.7
7830	3.910	3.910	-31.0	37.6	5.8	1.7	3.2	0.5	13.9	15.3	23.9
7862	3.970	3.970	-30.9	38.0	3.4	1.0	3.3	0.3	13.6	16.2	23.9
7895	4.030	4.030	-30.5	44.2	2.4	1.7	2.9	0.2	17.8	25.4	23.0
7906	4.050	4.050	-30.5	41.6	7.1	1.6	2.7	0.5	18.1	20.1	23.7
7912	4.060	4.060	-30.5	43.4	2.6	2.2	2.8	0.2	18.0	24.9	23.7
7919	4.074	4.074	-30.3	43.9	5.3	1.6	2.8	0.3	18.3	21.2	23.6
7934	4.100	4.100	-31.6	40.9	4.6	1.3	3.4	0.4	13.9	15.8	24.6
7961	4.150	4.150	-32.2	42.1	3.7	1.5	3.6	0.3	13.5	15.8	24.6
7988	4.200	4.200	-31.8	34.0	4.2	1.4	2.8	0.3	14.3	16.5	24.1
8016	4.250	4.250	-32.8	39.1	4.8	0.8	3.3	0.4	14.0	15.8	25.5
8043	4.300	4.300	-32.6	37.4	5.8	0.6	3.1	0.5	14.3	15.8	25.9
8071	4.350	4.350	-32.6	36.5	2.5	1.5	3.2	0.2	13.2	16.7	25.8
8076	4.360	4.360	-32.4	39.9	2.8	1.2	3.5	0.2	13.4	16.6	25.6
8082	4.370	4.370	-32.2	41.0	1.8	1.7	3.5	0.2	13.5	19.1	25.7
8087	4.380	4.380	-32.0	43.2	2.2	1.1	3.5	0.2	14.2	19.0	25.6
8098	4.400	4.400	-31.4	40.7	2.8	0.5	3.3	0.2	14.6	18.3	25.6
8125	4.450	4.450	-32.0	34.6	5.3	0.3	2.8	0.4	14.4	16.2	26.3
8153	4.500	4.500	-31.4	28.4	3.4	0.3	2.2	0.3	15.3	18.6	25.0
8180	4.550	4.550	-31.7	39.3	6.1	0.4	3.0	0.5	15.1	16.7	25.3
8208	4.600	4.600	-32.3	32.0	4.7	0.4	2.6	0.4	14.3	16.2	25.4
8235	4.650	4.650	-32.4	40.6	7.1	0.9	3.4	0.6	14.0	15.2	25.9
8262	4.700	4.700	-33.0	34.2	8.5	0.7	2.9	0.7	13.6	14.5	25.8
8290	4.750	4.750	-33.7	38.3	6.0	0.3	3.4	0.5	13.3	14.6	26.7

8316	4.798	4.798	-32.7	30.1	2.3	-0.1	2.5	0.2	14.0	18.6	25.8
8345	4.850	4.850	-33.2	38.9	2.2	1.3	3.5	0.2	12.9	16.9	26.7
8372	4.900	4.900	-33.6	33.5	2.3	0.8	3.0	0.2	13.2	17.1	26.5
8399	4.950	4.950	-33.2	36.3	2.0	1.3	3.3	0.2	12.8	17.3	27.2
8405	4.960	4.960	-34.4	43.8	2.6	1.1	3.4	0.2	15.2	19.7	28.0
8410	4.970	4.970	-33.2	44.3	2.0	1.6	3.7	0.2	14.0	19.4	27.5
8427	4.980	4.980	-32.9	42.4	1.8	1.1	3.7	0.1	13.5	21.4	27.2
8470	5.000	5.000	-33.7	40.7	1.9	1.0	3.3	0.2	14.6	21.3	27.8
8505	5.016	5.016	-31.6	40.0	2.0	1.1	3.1	0.2	14.8	18.2	24.6
8513	5.020	5.020	-32.7	41.7	2.9	1.4	3.6	0.2	13.4	17.2	25.7
8535	5.030	5.030	-32.4	40.6	3.8	1.5	3.4	0.3	13.9	16.1	25.4
8578	5.050	5.050	-32.3	39.2	3.2	1.5	3.3	0.3	13.8	15.5	26.2
8686	5.100	5.100	-33.1	37.2	0.5	1.1	3.3	0.0	13.0		26.4
8793	5.150	5.150	-32.1	22.2	5.6	1.1	2.0	0.5	13.0	15.3	26.4
8901	5.200	5.200	-32.7	38.3	1.9	1.3	3.2	0.2	13.8	17.3	27.5
9009	5.250	5.250	-32.7	37.7	2.5	1.2	3.5	0.2	12.7	16.1	27.1
9117	5.300	5.300	-33.6	35.8	2.3	1.1	3.3	0.2	12.8	17.3	27.4
9224	5.350	5.350	-32.8	30.7	1.8	1.3	2.7	0.2	13.4	17.2	26.8
9332	5.400	5.400	-32.6	38.7	6.2	1.2	3.6	0.6	12.4	13.8	26.8
9440	5.450	5.450	-32.9	37.5	1.4	1.5	3.5	0.1	12.6	17.3	27.2
9548	5.500	5.500	-32.1	34.8	2.2	0.6	3.5	0.2	11.7	14.8	26.7
9655	5.550	5.550	-32.6	35.0	1.5	0.9	3.5	0.2	11.6	16.0	26.7
9763	5.600	5.600	-32.5	31.5	1.7	1.4	3.2	0.2	11.3	16.1	25.8
9871	5.650	5.650	-32.7	32.8	2.0	1.1	3.3	0.2	11.6	15.0	27.0
9979	5.700	5.700	-32.4	35.8	1.8	0.5	3.6	0.2	11.5	16.1	27.2
10086	5.750	5.750	-32.4	32.9	1.7	0.9	3.2	0.2	11.9	15.0	27.7
10194	5.800	5.800	-31.7	32.6	2.0	0.6	3.4	0.2	11.2	14.3	26.9
10302	5.850	5.850	-30.3	28.9	1.2	0.5	3.0	0.1	11.1	17.9	26.3
10410	5.900	5.900	-30.0	24.6	1.6	0.4	2.5	0.2	11.3	16.5	26.0
10517	5.950	5.950	-29.9	22.5	1.6	0.4	2.2	0.2	11.8	15.3	26.3
10625	6.000	6.000	-30.5	20.5	1.0	0.4	2.2	0.1	11.1	17.4	26.7
10733	6.050	6.050	-29.0	16.5	1.3	-0.4	1.8	0.1	10.5	16.5	26.5
10797	6.080	6.080	-29.4	20.3	1.9	-0.3	2.2	0.2	10.9	15.8	26.9
10840	6.100	6.100	-28.8	17.2	1.1	-0.6	1.7	0.1	11.8	18.1	24.9
10884	6.120	6.120	-27.8	17.5	0.9	-0.2	1.9	0.1	10.8	20.8	26.1
10905	6.130	6.130	-28.1	17.7	1.1	0.3	1.9	0.1	10.9	17.7	26.3

10948	6.150	6.150	-28.0	13.5	0.7	0.4	1.5	0.1	10.7		26.6
11056	6.200	6.200	-27.8	16.2	0.7	1.1	1.8	0.1	10.4		26.8
11159	6.248	6.248	-28.3	15.9	1.2	0.4	1.8	0.1	10.4	15.3	26.7
11232	6.300	6.300	-27.9	17.2	1.0	0.3	2.0	0.1	10.3	16.6	26.5
11299	6.350	6.350	-27.2	11.6	1.1	0.4	1.3	0.1	10.1	14.5	26.7
11366	6.400	6.400	-27.1	2.8	2.3		0.3	0.3	9.6	11.1	27.4
11499	6.500	6.500	-25.2	2.4	2.0		0.3	0.3	9.3	10.6	
11499	6.500	6.500	-25.1	2.1	2.1		0.3	0.3	8.8	11.1	
11566	6.550	6.550	-25.2	2.3	2.0		0.3	0.3	9.2	10.6	
11566	6.550	6.550	-25.1	2.1	5.4		0.3	0.6	8.8	11.2	
11633	6.600	6.600	-30.0	10.5	4.1		1.2	0.4	10.3	12.8	28.5
11646	6.610	6.610	-29.4	12.4	1.7	0.7	1.3	0.2	11.4	14.3	28.1
11700	6.650	6.650	-28.9	14.4	1.9	0.6	1.6	0.2	10.7	13.3	27.0
11764	6.698	6.698	-28.6	14.8	2.3	0.1	1.7	0.2	10.4	13.2	27.0
12051	6.750	6.750	-29.4	11.4	2.4	0.9	1.2	0.3	10.8	13.6	28.1
12345	6.800	6.800	-28.9	14.0	2.6	0.7	1.5	0.3	11.1	12.9	28.0
12345	6.800	6.800	-28.7	15.1	1.7	0.6	1.6	0.2	10.8	13.1	27.8
12638	6.850	6.850	-29.0	16.4	2.2	0.9	1.9	0.2	10.1	13.9	26.6
12932	6.900	6.900	-28.9	17.9	1.9	0.7	1.9	0.2	11.1	13.9	28.3
13226	6.950	6.950	-28.1	13.5	1.3	0.5	1.5	0.1	10.8	16.3	27.7
13519	7.000	7.000	-27.8	14.6	1.8	-0.4	1.6	0.2	10.9	15.0	27.0
13637	7.020	7.220	-28.2	18.5	1.7	-0.1	1.9	0.2	11.3	14.7	27.8
13754	7.040	7.240	-27.1	17.2	1.4	-0.1	1.8	0.2	11.0	13.8	27.1
13813	7.050	7.250	-26.8	14.3	1.5	-0.4	1.7	0.2	9.9	13.5	27.3
14107	7.100	7.300	-26.7	14.3	1.7	-0.7	1.7	0.2	10.0	14.2	27.3
14165	7.110	7.310	-26.7	18.5	2.2	-0.3	2.0	0.2	10.7	12.7	27.1
14400	7.150	7.350	-25.8	14.5	1.6	-0.5	1.6	0.2	10.3	13.3	26.7
14694	7.200	7.400	-24.8	13.5	1.1	-0.7	1.6	0.1	10.0	14.6	26.3
14988	7.250	7.450	-26.2	2.5	1.1		0.3	0.1	9.4	13.4	27.3
14988	7.250	7.450	-26.0	2.6	2.3		0.3	0.2	9.0	13.0	
15281	7.300	7.500	-25.9	16.2	1.9	-0.5	1.8	0.2	10.6	13.9	27.1
15399	7.320	7.520	-25.3	16.1	2.1	-0.2	1.7	0.2	10.8	12.1	26.8
15575	7.350	7.550	-25.2	13.3	1.6	-0.0	1.6	0.2	9.9	13.8	27.2
15869	7.400	7.600	-23.8	10.3	2.1	-0.6	1.2	0.3	10.2	11.6	25.8
16151	7.448	7.648	-22.7	7.7	1.0	0.2	0.9	0.1	9.5	15.9	
16456	7.500	7.700	-22.9	1.9	0.3		0.2	0.0	9.8		25.6

CURRICULUM VITAE

Education:

2002 – 2005 **University of Saskatchewan**, Saskatoon, Saskatchewan, Canada

M.Sc., Geological Sciences

Topic – Climate change in western Ireland during the late glacial and Early Holocene using multiple isotope proxies from lake sediment.

1997 – 2002 **University of Tennessee**, Knoxville, Tennessee

B.S., Honors Geology, *Magna Cum Laude*, GPA 3.72/4.00

B.F.A., Studio Art, concentration in ceramics, *Magna Cum Laude*

Work Experience:

2002 – 2005 **University of Saskatchewan**, Saskatoon, Saskatchewan, Canada

***Graduate Teaching Assistant**, Geological Sciences*

- Prepared and taught Isotope Geochemistry Tutorial sessions
- Prepared and taught Geochemistry Tutorial sessions
- Prepared and instructed laboratory exercises in sedimentology and advanced mineralogy
- Prepared and led field exercises in lake coring and water sampling in the Yucatan, Mexico

Graduate Student Research Experience and Skills

- Conducted field work in lake coring, water sampling, tree coring, and modern organics in many parts of Ireland
- Conducted stable isotope analyses of lacustrine calcite (C,O), lacustrine organic sediment (C,N), lacustrine sediment cellulose (O), surface waters (O,H), and tree cellulose (C,O)
- Strong hands-on and maintenance experience on mass spectrometers (Thermo Finnegan) and peripheral devices (TC/EA, EA, Kiel III, Conflow)
- Skilled in various computer programs including Adobe Illustrator, Dreamweaver, Photoshop, Excel, Word, and Powerpoint.
- Webpage development and maintenance for Forum for Geoscience Education and Outreach Center

2002 **Keck Geology Consortium,** Carleton College, Minnesota

Graduate Student Field Assistant

- Assisted student researchers in field sampling in Ireland including soil, sediment and water sampling, logging and preservation techniques
- Assisted students in preparation and stable isotope analyses of soil and sediment cores at the University of Saskatchewan

2001 – 2002 **University of Tennessee**, Knoxville, Tennessee
Undergraduate Research Assistant

- Conducted stable isotope analyses of calcite (C,O) and organics (C) on sediments from soil sequences in southeast Texas

Awards and Achievements:

2005	**Best Graduate Student Poster**, Western Inter University Geological Society Annaul Meeting
2004	**Student Travel Award,** Geological Society of America
2004	**College of Graduate Studies and Research Travel Grant**, College of Graduate Studies, University of Saskatchewan
2004	**Graduate Student Fellowship**, College of Graduate Studies, University of Saskatchewan
2004	**Student Travel Award,** University of Saskatchewan, Office of the President
2004	**Graduate Student Research Grant**, Geological Society of America
2003	**Graduate Student Fellowship**, College of Graduate Studies, University of Saskatchewan
2003	**Graduate Student Research Grant**, Geological Society of America
2002	**Graduate Student Scholarship**, College of Graduate Studies, University of Saskatchewan
2002	**Outstanding Senior Award**, Department of Geological Sciences, University of Tennessee
2002	**"Coffee Cup Award"** for Highest Undergraduate GPA in Geological Sciences, University of Tennessee
2002	**Travel Grant**, Southeastern Geological Society of America
2001	**Don Jones Geology Field Camp Scholarship**, University of Tennessee
2001	**Knoxville Gem & Mineral Society Award for Excellence**, in Mineralogy
2000	**James G. Walls Award**, Superior Student in Introductory Geology
1998	**Phi Eta Sigma National Honor Society,** University of Tennessee
1997	**Golden Key National Honor Society**, University of Tennessee

Publications:

Diefendorf, A.F., and Patterson, W.P. (*in press*). Survey of stable isotope values in Ireland surface waters. *Journal of Paleolimnology*.

Diefendorf, A.F., Patterson, W.P., Mullins, H.T., Tibert, N., and Martini, A. (*in review.*). High Frequency Climate Variability during the Late Glacial to mid-Holocene (16,800 to 5500 calendar years BP) at Lough Inchiquin, Ireland: Evidence from Oxygen Isotope Values of Lacustrine Sediment.

Diefendorf, A.F., Patterson, W.P., and Holmden, C., (*in prep.*). Landscape and climate change from 16,500 to 5,300 calendar years before present at Lough Inchiquin, western Ireland inferred from a multiproxy study of lake sediments.

Presentations with Published Abstracts:

Diefendorf, A.F., and Patterson, W.P., 2005. Spatial Variation of Stable Isotope Values of Modern Irish Surface Waters: A Foundation for Multi-proxy Paleoclimate Investigations of Ireland.

Western Inter-University Geological Conference. Saskatoon, SK, Canada.

Ogilvie*, P.L., **Diefendorf, A.F.,** Patterson, W.P., Holmden, C., and Mullins, H.T., 2005. Multiproxy Stable Isotope Study of Holocene Climate variability at Lough Gallaun, Western Ireland. Western Inter-University Geological Conference. Saskatoon, SK, Canada.

Dietrich, K.A., Patterson, W.P., Holmden, C., and **Diefendorf, A.F.,** 2005. A Survey of Stable Isotopes in Modern Surface Waters of Iceland. Western Inter-University Geological Conference. Saskatoon, SK, Canada.

Diefendorf, A.F., and Patterson, W.P., 2004. Stable Isotopes in Modern Irish Surface Waters: A Basis for Paleoclimate Investigations of Ireland. Geological Society of America Annual Meeting, Denver, CO.

Ogilvie*, P., **Diefendorf, A.F.**, Patterson, W.P., Holmden, C., and Mullins, H.T., 2004. Multiproxy Study of Late Pleistocene/Holocene Climate Variability at Lough Gallaun, Western Ireland from Stable Isotopes of Lacustrine Marl and Organic Sediment. Geological Society of America Annual Meeting, Denver, CO.

Dietrich, K., Patterson, W.P., Holmden, C., and **Diefendorf, A.F.**, 2004. A Survey of Stable Isotopes in Modern Surface Waters of Iceland. Geological Society of America Annual Meeting, Denver, CO.

Diefendorf, A.F., Patterson, W.P., Mullins, H.T., Martini, A., and O'Connell, M. 2003. High-Resolution Holocene Climate Variability at Lough Inchiquin, Western Ireland: Evidence from Stable Carbon and Oxygen Isotope Values of Lacustrine Sediment. Geological Society of America Annual Meeting, Seattle, WA.

Diefendorf, A.F., Patterson, W., Mullins, H., and Martini, A., 2003. High-resolution Holocene Climate Variability: Evidence from Stable Isotope Values of Lacustrine Carbonate from Western Ireland. Geological Association of Canada Annual Meeting. Vancouver.

Diefendorf, A.F., and Patterson, W., 2003. Late Glacial to Mid-Holocene Climate Change in Western Ireland: Evidence from High-Resolution Stable Isotope Record of Lacustrine Marl. 16th Annual Keck Research Symposium in Geology Proceedings, Keck Geology Consortium. Beloit College, Beloit, WI.

Diefendorf, A.F., and Mora, C.I., 2002. Tracking Quaternary Ecosystem Shifts in a Modern Vertisol Climosequence, Texas Coastal Prairie. North-Central Section and Southeastern Section, Geological Society of American Joint Annual Meeting, Lexington, KY.

Mora, C.I., Miller, D.L., **Diefendorf, A.F.**, and Driese, S.G., 2002. Stable Isotopes, Climate and Time: Isotopic Trends in a Vertisol Climosequence and Chronosequence from the Texas Gulf Coastal Prairie, USA. Sixth International Symposium on the Geochemistry of the Earth's Surface East-West Center, Honolulu, HI.

Mora, C. I., Miller, D.L., **Diefendorf, A.F.**, Stiles, C.A., and Driese, S.G., 2002. Climate-Isotope Relationships in a Modern Vertisol Climosequence, Coastal Texas. Geological Society of America Annual Meeting, Denver, CO.

* Co-supervising undergraduate student with Dr. Patterson.

Primary Advisors:

- **William P. Patterson (Graduate Advisor, University of Saskatchewan)**
- **Claudia Mora (Undergraduate thesis advisor, University of Tennessee)**

Professional Affiliations:

- American Geophysical Union
- Geological Society of America
- American Institute of Professional Geologists
- Geological Association of Canada

Contact information:

e-mail: aaron.diefendorf@usask.ca
website: www.diefendorf.centergeo.org